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BORON FLUORIDE AND ITS COMPOUNDS AS CATALYSTS IN ORGANIC CHEMISTRY

by

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INTRODUCTION

THE present monograph deals with the use of boron fluoride as a catalyst in organic chemistry and also with a number of its derivatives and coordination compounds.

Boron fluoride and many of its compounds are very active catalysts in numerous organic and petroleum chemical syntheses (polymerization, alkylation, isomerization, condensation, degradation, etc.) where acid catalysts are used.

Such varied use of boron fluoride as a catalyst is made clear by the structure of the electron atmosphere of boron and by the properties of the molecule BF_3 as a whole, which is very prone to complex formation, this being an important factor in the formation of catalytically active structures in acid catalysis.

Organic synthesis is widely used in different branches of the national economy, and is the basis of the industrial production of a large number of compounds which not only replace natural products but also gain independent new applications. Such compounds include the basic materials for the manufacture of synthetic rubber, synthetic fibres, plastics, synthetic detergents, toxic substances, plant growth stimulants, vitamins, colouring matters, nitro-compounds, solvents, synthetic alcohols, acids, ketones, halogen derivatives, new medicinal preparations and many other substances of the organic synthetic industry. The industrial manufacture on a large scale of the products indicated was made possible by the chemical treatment of coal and petroleum and the introduction of new catalysts into chemical processes. In the petroleum processing industry all the methods of synthesis of the high octane components of motor fuels (polymerization of olefines with subsequent hydrogenation of the dimers, alkylation, isomerization, dehydrocyclization, etc.) are carried out catalytically and the same applies to the production of artificial liquid fuel.

In this book an attempt has been made to summarize all the available knowledge about a remarkable compound, boron fluoride, which possesses noteworthy properties. Chemists in the most varied fields of specialization are interested in boron fluoride. Some are attracted by its unusual physical properties, others are interested in its remarkable capacity for forming molecular compounds with different inorganic and organic substances, and a third group is interested in the high catalytic activity of boron fluoride in a series of reactions.

As long ago as 1873 V. Goryanov and A. M. Butlerov brought about the polymerization of *iso*butylene to di-*iso*butylene in the presence of boron fluoride, thereby laying the foundations for the production of high octane fuel. In 1935 the reaction of the alkylation of isoparaffins with olefines was carried out for the first time, also with catalysts based on boron fluoride.

As a catalyst boron fluoride began to attract the attention of organic chemists about 1930. It is a particularly active catalyst in alkylation, condensation, polymerization and isomerization reactions.

The catalytic action of boron fluoride in certain reactions is similar to the action of mineral acids (H_2SO_4, H_3PO_4 and HF) but in some cases it approximates to the catalytic action of the halogen compounds of metals. Molecular compounds of boron fluoride possess different catalytic activity. Some, such as, for example, $H_2O . BF_3$ and $H_3PO_4 . BF_3$ are more active than free BF_3; others act more mildly, as for example $(C_2H_5)_2O . . BF_3$. They are quite rightly considered as individual catalysts and their use is dependent on the type of reaction. This makes possible a wide choice of catalysts based on boron fluoride for particular reactions.

Catalysts based on boron fluoride are more active in many reactions than mineral acids and halogen compounds of metals, and at the same time do not give rise to undesirable side reactions: the extremely destructive changes which are observed when aluminium chloride is used, or even sulphonation and fluorination when sulphuric acid and anhydrous hydrogen fluoride are employed.

Many syntheses in which boron fluoride is used have become firmly established in the practice of organic chenistry; boron fluoride has for many years been widely employed in certain industrial processes and in scientific research work.

The use of boron fluoride was already advocated by the authors of the present monograph at the first stages of its introduction as a catalyst in organic chemistry, processes for the alkylation of isoparaffins and aromatic hydrocarbons by means of olefines in the presence of molecular compounds of boron fluoride have been worked out, the low molecular and high molecular polymerization of olefines in the presence of different catalysts based on boron fluoride has been studied, and also the alkylation of phenols and organic acids. Molecular compounds of boron fluoride with phosphoric acids, which are particularly outstanding in their catalytic action, have been prepared, characterized, and studied in many reactions for the first time by the authors; in addition, general mechanisms of the catalytic action of boron fluoride compounds have been formulated.

The authors trust that the present monograph may be used as a textbook on boron fluoride for specialists working in the field of organic chemistry, and that it will contribute to a still wider introduction of this catalyst into industry.

CHAPTER I

METHODS FOR THE PREPARATION AND RECOVERY OF BORON FLUORIDE

1. METHODS FOR THE PREPARATION OF BORON FLUORIDE

Boron fluoride, as D. I. Mendeleev [1] recorded, is formed "in the majority of cases when boron and fluorine compounds are brought together." In laboratory conditions boron fluoride may be obtained by the following methods.

(1) By heating a mixture of calcium fluoride and boric anhydride to a white heat (at a temperature of 900—1200°) [1—3]:

$$3CaF_2 + 2B_2O_3 \rightarrow 2BF_3 + Ca_3B_2O_6$$
$$3CaF_2 + B_2O_3 \rightarrow 2BF_3 + 3CaO$$

(2) By heating sodium fluoride and boric anhydride to a high temperature (fusion) [4]:

$$6NaF + B_2O_3 \rightarrow 2BF_3 + 3Na_2O$$

(3) By heating lead fluoride, powdered boric anhydride and aluminium [5]:

$$3PbF_4 + 2B_2O_3 + 2Al \rightarrow 4BF_3 + 3PbO + Al_2O_3$$
$$3PbF_4 + B_2O_3 + 2Al \rightarrow 2BF_3 + 2AlF_3 + 3PbO$$

(4) Boron fluoride is also obtained by the thermal dissociation of fluoroborates:

(a) sodium fluoroborate decomposes on heating into boron fluoride and sodium fluoride [6] according to the equation:

$$NaBF_4 \rightarrow BF_3 + NaF$$

(b) in the same way potassium fluoroborate decomposes at a temperature of 600—700° [7]:

$$KBF_4 \rightarrow BF_3 + KF$$

it is desirable to carry out the reaction *in vacuo*;

(c) by heating calcium fluoroborate to 300—500° [8]:

$$Ca(BF_4)_2 \rightarrow 2BF_3 + CaF_2$$

This reaction is used for recovering boron fluoride from reaction mixtures in which it occurs in the form of hydrates or etherates. For this purpose the boron fluoride contained in the reaction mixture is first converted into calcium fluoroborate according to the reaction

$$2BF_3 + CaF_2 \rightarrow Ca(BF_4)_2$$

The latter separates in the form of a precipitate.

(5) Pure boron fluoride not containing any impurities but nitrogen is obtained by the decomposition of a diazonium fluoroborate [9]:

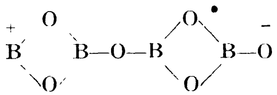
$$ArN_2BF_4 \rightarrow BF_3 + ArF + N_2$$

The boron fluoride is separated from the nitrogen by deep freezing or by adsorption on a suitable substance with the formation of molecular compounds.

(6) By heating potassium fluoroborate to fusion (518°) in admixture with boric anhydride [10]:

$$KBF_4 + 2B_2O_3 \rightarrow BF_3 + KFB_4O_6$$

Hellriegel [10] assumes that the boric anhydride in this reaction reacts in the form of a dipolar molecule of the structure



This method is convenient for the preparation of both small and large quantities of pure boron fluoride, in addition to which the process may be conducted in a glass apparatus and, when pure starting materials free from SiO_2 are used, even in an iron reaction vessel.

(7) Boron fluoride is obtained by heating a mixture of calcium fluoride boric anhydride and concentrated sulphuric acid [11—17]:

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$
$$3CaF_2 + B_2O_3 + 6H_2SO_4 \rightarrow 2BF_3 + 3Ca(HSO_4)_2 + 3H_2O$$

This is the oldest and most widely known method in laboratory practice. Even Davy [11], one of the first investigators of boron fluoride, used it, and the method is frequently used by many research workers at the present time. The reaction is usually carried out using a considerable excess of boric anhydride (to avoid the formation of hydrogen fluoride) and a large excess of sulphuric acid. (It is better to use 1—3 per cent oleum.)

As our experience of many years' standing shows, boron fluoride is conveniently obtained by this method in the following way: 36—40 g fluorspar and 20 g boric anhydride, ground to powder and well mixed, are placed in a 500 ml Wurtz flask, to which is added 200—210 g sulphuric acid, sp. gr. 1·84. The mixture is heated very slowly with frequent shaking. The gaseous boron fluoride which is given off is passed directly into the reaction mixture, or into absolute ethyl ether, if boron fluoride is used in the form of etherate. Heating is continued to a temperature of 200—250°, i.e. until hydroxyfluoroboric acid $(HO)_2BF$ [18] begins to distil in the form of a viscous, clear liquid which blocks up the outlet tube. The maximum yield of boron fluoride is about 70—75 per cent when oleum is used.

Some investigators [14, 19] recommend first dissolving the powdered boric anhydride in sulphuric acid, and then introducing the calcium fluoride and collecting the SO_3 and HF which are evolved at the same time in special traps.

I. G. Ryss and E. M. Polyakova [20] studied the influence of temperature, concentration and excess of sulphuric acid on the yield of boron fluoride in this method of preparation. In experiments with oleum, in order to eliminate the violent frothing of the reaction mixture and to prevent the possibility of its being ejected, these authors first introduced about one third of the oleum into the reaction flask, added the mixture of calcium fluoride and boric anhydride, mixed the substances thoroughly, placed the flask on a heated bath and added the remaining portion of oleum over a period of 10—15 min. As the results of the experiments show (Table 1), a rise of temperature from 150 to 180°, an increase in the excess of sulphuric acid up to 200 per cent and a rise in its concentration exert a favourable influence on the course of the process. However, in spite of everything the maximum yield of boron fluoride does not exceed 66·6 per cent of the theoretical.

Table 1. *Decomposition of a mixture of* CaF_2 *and* B_2O_3 *with sulphuric acid with the formation of boron fluoride* [20]

Temperature (°C)	Concentration H_2SO_4 (%)	Excess H_2SO_4 (% of stoichiometric quantity)	Total yield of BF_3 (%)
150	92·0	100	8·6
150	105·9	100	22·4
180	92·0	200	35·9
180	105·9	100	64·4
180	105·9	200	66·6

(8) According to facts given in certain patents [21], boron fluoride is obtained by heating calcium fluoride with boric and sulphuric acids

$$3CaF_2 + 2H_3BO_3 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 6H_2O$$

but this reaction must be carried out at a higher temperature than is the case with boric anhydride, and it must be in the presence of dehydrating substances. The yield of boron fluoride in this case is considerably lower than when boric anhydride is used, which is explained by the formation during the reaction of a large quantity of water which absorbs the boron fluoride.

(9) A method has been proposed for preparing boron fluoride by heating a mixture of calcium fluoride, boric anhydride and sulphur trioxide [22]:

$$3CaF_2 + B_2O_3 + 3SO_3 \rightarrow 2BF_3 + 3CaSO_4$$

The reaction is carried out in a rotating autoclave at 250° and a pressure of 20—36 atm. This process has the disadvantage that the calcium sulphate forms a solid mass which is difficult to remove from the reaction vessel.

(10) Boron fluoride is obtained by heating fluoroborates with boric anhydride and sulphuric acid :

(a) by heating $NaBF_4$ (300 g) or NH_4BF_4 (287 g) and B_2O_3 (50 g) in 300 ml concentrated H_2SO_4 [23]:

$$6NaBF_4 + B_2O_3 + 6H_2SO_4 \rightarrow 8BF_3 + 6NaHSO_4 + 3H_2O$$

(b) similarly by heating potassium fluoroborate and boric anhydride with concentrated sulphuric acid [24—31]:

$$6KBF_4 + B_2O_3 + 6H_2SO_4 \rightarrow 8BF_3 + 6KHSO_4 + 3H_2O$$

yield 82 per cent.

I. G. Ryss and E. M. Polyakova [20] studied the effect of temperature, concentration and excess of sulphuric acid and excess of boric anhydride on this process and found that when 95·5 per cent H_2SO_4 is used in the reaction with a 50 per cent excess of B_2O_3 and a 200 per cent excess of H_2SO_4, a copious condensation of boron fluoride hydrate $BF_3 . nH_2O$ is observed in the upper part of the reaction flask and the yield of BF_3 amounts in all to 9·5 per cent at 150° and 47·7 per cent at 180°. When 99·5 per cent H_2SO_4 is used, boron fluoride hydrate is formed in insignificant quantities and the yield of BF_3 at 150 and 180° is 42·6 and 64·0 per cent respectively.

In the reaction with oleum (105·9 per cent H_2SO_4) at 180° dry BF_3 is obtained in a yield of 79·1 per cent More than 200 per cent excess of oleum scarcely increases the yield of BF_3; a 50 per cent excess of boric anhydride at 180° and a 200 per cent excess of oleum decreases the yield of BF_3 from 82 to 75·6 per cent, probably as a result of the formation of $BF_3 . B_2O_3$ in the liquid phase. For carrying out the reaction some investigators [26] recommend, as in the method using CaF_2, first dissolving boric anhydride in sulphuric acid, and then gradually introducing potassium fluoroborate in order to prevent the formation of hydrogen fluoride. They also suggest carrying out the decomposition with hot sulphuric acid [27] with the object of decreasing the amount of it.

(11) Boron fluoride may be obtained from boric anhydride, cryolite and sulphuric acid [32]:

$$2Na_3AlF_6 + 2B_2O_3 + 9H_2SO_4 \rightarrow 4BF_3 + 6NaHSO_4 + Al_2(SO_4)_3 + 6H_2O$$

(12) In industry boron fluoride has been prepared since 1939 by heating BF_3—metal oxide complexes with sulphuric acid [33], for example:

$$Na_2O \cdot 4BF_3 + H_2SO_4 \rightarrow 4BF_3 + Na_2SO_4 + H_2O$$

The process is carried out in two stages: in the first the complex $Na_2O \cdot 4BF_3$ is obtained, but in the second stage this complex is treated with sulphuric acid in order to liberate the boron fluoride. In factory conditions the complex $Me_2O \cdot 4BF_3$ is prepared by the following methods [33]:

(a) from borax and liquid hydrofluoric acid:

$$Na_2B_4O_7 \cdot 10H_2O + 12HF \rightarrow Na_2O \cdot 4BF_3 + 16H_2O$$

the borax is gradually added to the hydrofluoric acid, and then after the reaction is over, the temperature is raised to evaporate the water;

(b) from ammonium bifluoride and boric acid or ammonium fluoride and boric anhydride:

$$6NH_4HF_2 + 4H_3BO_3 \rightarrow (NH_4)_2O \cdot 4BF_3 + 4NH_3 + 11H_2O$$
$$12NH_4F + 2B_2O_3 \rightarrow (NH_4)_2O \cdot 4BF_3 + 10NH_3 + 5H_2O$$

After the reaction has been carried out the water and ammonia are removed by heating.

The subsequent stage is carried out in a second reaction vessel into which the product of the first stage (BF_3—metal oxide complex) and sulphuric acid containing 20 per cent SO_3 are fed. The reaction is started by heating, after which the rate of evolution of boron fluoride is controlled by gradually increasing the temperature. As the gas is formed it enters into gasholders, from which it is pumped by means of a compressor into steel cylinders under a pressure of 140 atm. The consumption of sulphuric acid is about eight times less than in laboratory method (7) [34].

(13) It has been recommended that boron fluoride be prepared from boric acid and hydrogen fluoride [35]:

$$H_3BO_3 + 3HF \rightarrow BF_3 \cdot 3H_2O \rightarrow BF_3 + 3H_2O$$

The hydrated boron fluoride complex is broken down by a two-stage distillation at atmospheric and reduced pressure.

At the same time, fluoroboric acid is also formed. When concentrated aqueous solutions of this are heated it decomposes with the evolution of boron fluoride and hydrogen fluoride:

$$HBF_4 \rightarrow BF_3 + HF$$

(14) There are indications that boron fluoride is obtained in good yield by heating fluorosulphonic acid and boric acid under pressure in a closed reaction vessel [36]:

$$3HOSO_2F + H_3BO_3 \rightarrow BF_3 + 3H_2SO_4$$

The sulphuric acid which is formed as a secondary product is used for the preparation of fluorosulphonic acid and for first dissolving the boric acid in order to facilitate its introduction into the reaction vessel which is under pressure.

(15) Boron fluoride may be prepared by fluorinating boron chloride with antimony trifluoride in the presence of $SbCl_5$ as a catalyst at temperatures from 0 to −78° [37]:

$$BCl_3 + SbF_3 \xrightarrow{SbCl_5} BF_3 + SbCl_3$$

(16) In the silicate industry, when vitreous enamels and borosilicate glasses are fused, vapours are formed which contain boron fluoride, which may be collected by absorbing it in sulphuric acid at 21—28° and a pressure of 1·5—15 atm [38]. Pure boron fluoride is then liberated when the sulphuric acid solution is heated.

In many methods the production of boron fluoride is accompanied by the formation of small quantities of secondary products (HF and SiF_4), which occur in it as impurities. When boron fluoride is used as a catalyst in laboratory conditions, there is in most cases no need to separate the aforesaid impurities because they have no disadvantageous effect on the catalytic activity of boron fluoride. On the other hand, the hydrogen fluoride present in the BF_3 acts as a good promoter in many reactions. Therefore the gaseous boron fluoride formed is passed directly, without any preliminary purification, into the reaction mixture.

For the preparation of chemically pure boron fluoride different methods of purification are used, depending on the nature of the impurities contained in it. To separate the SiF_4 the gases formed during the reaction are passed through a column filled with NaF and fused B_2O_3 [16], or are liquefied by cooling in liquid air and fractionated *in vacuo*. Boron fluoride and silicon fluoride (b. p. −101 to −77°) may be separated by means of a good fractionating column at one distillation [39, 40].

Hydrogen fluoride is removed by passing the gaseous boron fluoride through concentrated sulphuric acid saturated with boric anhydride, or through a column of NaF and B_2O_3 [16].

2. A BRIEF EVALUATION OF THE METHODS FOR THE PREPARATION OF BORON FLUORIDE

A careful analysis of the data given in the literature and also many years' experience in our laboratories indicate that at present the acid methods are the most convenient and economical. Of these methods both for laboratory and for technical use the four following methods may be recommended:

(1) $6KBF_4 + B_2O_3 + 6H_2SO_4 \rightarrow 8BF_3 + 6KHSO_4 + 3H_2O$
(2) $3CaF_2 + B_2O_3 + 6H_2SO_4 \rightarrow 2BF_3 + 3Ca(HSO_4)_2 + 3H_2O$
(3) $Na_2O \cdot 4BF_3 + H_2SO_4 \rightarrow 4BF_3 + Na_2SO_4 + H_2O$
(4) $H_3BO_3 + 4HF \rightarrow BF_3 + HF + 3H_2O \rightleftarrows HBF_4 + 3H_2O \rightarrow BF_3\uparrow +$
$+ HF\uparrow + 3H_2O$

By the first method boron fluoride is obtained in a yield of 80—82 per cent [20]. Its main disadvantage is the unavoidability of the preliminary superfluous stage, the preparation of KBF_4 from boric acid and 20 per cent [20] or 47 per cent [41] hydrofluoric acid (yield 86—93 per cent). However, the disadvantage is compensated for by the fact that this method requires only the stoichiometric quantity of boric anhydride (with a 200 per cent excess of oleum) and gives a high yield of boron fluoride.

The second method enables boron fluoride to be obtained in a maximum yield of 65 per cent of the theoretical, but requires a 50 per cent excess of boric anhydride, by which it rather concedes to the first.

The third method, which is already used in industry [33], would seem very simple, but to carry it out it is necessary first to prepare a complex from borax or ammonium bifluoride. In our conditions it will probably be the least economical because in the U.S.S.R. borax is obtained from technical boric acid.

The fourth method is quite convenient but requires hydrogen fluoride and the separation of boron fluoride and hydrogen fluoride.

Boron fluoride, prepared on an industrial scale [42], is stored under pressure in steel cylinders.

Steel cylinders and pipelines may be used for storing and transferring dry BF_3; copper tubes and brass fittings may also be used for this purpose. As regards moist boron fluoride, copper, ebonite. hard paraffin and glass are quite resistant. Iron is completely decomposed by moist boron fluoride. Litharge dispersed in oil and a viscous oil containing graphite are used to seal the tubes. For filling the various seals asbestos with graphitized oil are used.

Mercury, purified mineral oil, direct distillation benzine and kerosene, and also carbon tetrachloride are used as suitable liquids for manometers and low-pressure gasholders in which BF_3 is stored.

3. METHODS OF RECOVERY OF BORON FLUORIDE

One of the advantages of boron fluoride over catalysts of similar type is the possibility of its recovery in many cases from the reaction mixture.

All methods of recovering BF_3 are based on its capacity for giving molecular compounds with different organic and inorganic substances. Such compounds may in certain conditions easily liberate boron fluoride.

Since boron fluoride is very difficultly soluble in hydrocarbon mixtures (in polymerization products of olefines the solubility of BF_3 is 5—5·5 per cent) and forms unstable molecular compounds with hydrocarbons, it may be removed quantitatively from such mixtures by simple heating.

Hydrocarbon mixtures obtained in polymerization, alkylation or isomerization reactions and containing boron fluoride are usually subject to slight heating. The gas evolved, being a mixture of boron fluoride and low-boiling saturated and unsaturated hydrocarbons, is passed through absorbents or solvents capable of combining with boron fluoride. The molecular compounds formed then decompose yielding boron fluoride. Diaryl ketones, for example benzophenone [43, 44], and diaryl or arylalkyl ethers may be used as these absorbents [45]. They absorb boron fluoride well, but in contrast to dialkyl ethers they easily give off boron fluoride again at comparatively low temperatures. For example, anisole easily absorbs boron fluoride at room temperature, but at 100—150° it splits it off quantitatively:

$$C_6H_5OCH_3 . BF_3 \underset{20-25^\circ}{\overset{100-150^\circ}{\rightleftarrows}} C_6H_5OCH_3 + BF_3$$

To guarantee a uniform evolution of BF_3 it is recommended that the molecular compound $C_6H_5OCH_3 . BF_3$ be added to a heated flask in small portions from a dropping funnel. From 100 g $C_6H_5OCH_3 . BF_3$ 35—38 g pure boron fluoride is obtained.

Liquid anhydrous hydrogen fluoride [46—49] and liquid alkyl sulphides or mercaptans [50] are good selective absorbents of boron fluoride.

It is possible to split off boron fluoride from the majority of molecular compounds by means of ammonia. Many patents therefore recommend that BF_3 which has been used as a catalyst in condensation, polymerization, alkoxylation, acyloxylation and other reactions be recovered by treating the reaction mixtures with ammonia or amines [51]. The stable complexes, for example $BF_3 . NH_3$, hereby formed, which are insoluble in organic mixtures, are separated and decomposed with sulphuric acid at 190—200° according to the reaction.

$$2BF_3 . NH_3 + H_2SO_4 \xrightarrow{190-200^\circ} BF_3 + (NH_4)_2SO_4$$

Up to 75 per cent of the boron fluoride [52, 53] can be recovered by this method.

In those cases when boron fluoride is found in the reaction products in the form of molecular compounds with water [54—56], carboxylic acids, alkyl ethers [57—61] or hydrofluoric acid [62], it may be recovered:

(a) by a two-stage distillation at different pressures;

(b) by combining it with certain metal halides (NaF, LiF, CaF_2, etc.) to form fluoroborates and by decomposing the latter at high temperatures with the liberation of BF_3.

In the first case, the water and acid are distilled off under reduced pressure, then the pressure in the system is brought to normal, the temperature is raised and the free BF_3 distilled off. At the same time, the decomposition of some molecular compounds is accompanied by side reactions, as for example,

$$3BF_3 . H_2O \rightarrow 2BF_3 + 3HF + H_3BO_3$$

in consequence of which the recovery involves considerable losses of BF_3.

The process may also be carried out at atmospheric pressure. For example, calcium fluoride is added to the molecular compound $BF_3 . 2CH_3COOH$ or $BF_3 . nH_2O$ and the mixture heated on an oil bath at 100—250° until all the acid or water is driven off. The residue, which consists of calcium fluoroborate, decomposes at 300—500°:

$$2BF_3 . 2CH_3COOH + CaF_2 \xrightarrow{-4CH_3COOH} Ca(BF_4)_2 \xrightarrow{300-500^\circ} 2BF_3 + CaF_2$$

$$2BF_3 . 2H_2O + CaF_2 \xrightarrow{-4H_2O} Ca(BF_4)_2 \xrightarrow{300-500^\circ} 2BF_3 + CaF_2$$

The aqueous solutions of the reaction mixture may be treated with potassium, rubidium or caesium fluorides, and in this way the BF_3 can be converted into the fluoroborates of these metals [63]. These salts can be separated, dried and then decomposed with the evolution of boron fluoride by heating with boric anhydride and sulphuric acid, as described in method 10(b). In some cases BF_3 may be recovered from the reaction mixture in the form of molecular compounds by ordinary rectification, and such compounds may be used as catalysts without decomposition. In the addition of acetic acid to *cyclo*hexene in the presence of $BF_3 . O(C_2H_5)_2$, S. V. Zavgorodnii recovered the catalyst in the form $BF_3 . 2CH_3COOH$ in a yield of about 60 per cent and used it again for the same reaction. Since the molecular compound of boron fluoride with acetic boils at a lower temperature than *cyclo*hexyl acetate (173—175°), the complex $BF_3 . 2CH_3COOH$ was first distilled from the reaction mixture at 136—143°, and the *cyclo*hexyl acetate was separated from the residue by the usual method.

In the addition of acetic acid to propylene in the presence of BF_3 and HF [64], *iso*propyl acetate was first distilled from the reaction mixture because it boils at a lower temperature than the complex $BF_3 . 2CH_3COOH$; fresh reagents were added to this complex which remained in the flask, and the reaction was carried out again with the same yield of ether as in the presence of BF_3 and HF.

It has been suggested that a method of recovering BF_3, based on its capacity of easily forming stable molecular compounds with organic compounds containing oxygen, sulphur and nitrogen, be used for separating these substances from mixtures by combining them into complexes with BF_3 and subsequently decomposing the complexes. Acetic acid and propionic acid are thus isolated, having been synthesized from olefines and carbon monoxide in the presence of BF_3 [65, 66].

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CHAPTER II

PHYSICAL AND CHEMICAL PROPERTIES OF BORON FLUORIDE AND ITS DERIVATIVES

1. PHYSICAL PROPERTIES

Boron fluoride, described as a remarkable compound by D. I. Mendeleev [1], is a colourless, non-inflammable gas which does not support combustion, and is 2·3 times heavier than air. On mixing with moist air it forms a dense, white smoke as a result of combination with water vapour. At —110° boron fluoride condenses to a mobile, colourless liquid which on cooling to —160° solidifies to a white mass [2] melting, according to different literature sources, at: —126° [3]; —127° [4]; —127·1° [5]; —128° [6]. For boiling point the values — 99° [4], —100·4° (760 mm) [5] and —101° [6] are given. The critical temperature and pressure of boron fluoride are equal to —12·25° and 49·2 atm [7].

The vapour pressure of BF_3 in the temperature range from —49·25° to —12·25° is expressed by the equation

$$\log p = 5{\cdot}1009 - \frac{889{\cdot}6}{T}$$

where p is the pressure in atmospheres, and T is the absolute temperature.

In Table 2 vapour pressure data of BF_3 above the boiling point (—100·4°) are given [7].

The vapour pressure of BF_3 below the boiling point may be expressed by the equation [6]

$$\log p = 8{\cdot}828 - \frac{1023{\cdot}5}{T}$$

where p is the vapour pressure in millimetres of mercury.

Table 2. Saturated vapour pressure of boron fluoride

Temperature (°C)	Pressure (atm)	Temperature (°C)	Pressure (atm)
—12·25	49·0	—52·2	11·54
—14·60	45·5	—54·4	10·00
—19·95	38·6	—57·8	9·93
—29·96	27·9	—63·3	7·50
—39·20	20·5	—73·3	4·61
—49·25	13·8	—100·4	1·00

The density of solid boron fluoride [6, 8] is: $d^{-125} = 1{\cdot}796$, $d^{-130} = 1{\cdot}87$, $d^{-188} = 1{\cdot}98$, $d^{-270} = 2{\cdot}04$; the coefficient of thermal expansion [9] is $3{\cdot}4 \times 10^{-4}$. The density of liquid boron fluoride at the boiling point is 1·60 [6, 8]; according to other data: 1·58 [9] and 1·57 [10]. The density of BF_3 in the liquid state at different temperatures may be expressed by the equation

$$d = 2{\cdot}6999 - 0{\cdot}00642\,T$$

where T is the absolute temperature.

The coefficient of thermal expansion in the liquid state is $3{\cdot}4 \times 10^{-4}$ [6].

The density of gaseous boron fluoride at 20° and a pressure of 760 mm mercury is 3·0 g/l.; at 0°, 3·07666 g/l. and at −88° 4·613 g/l.

The presence of isotopes ^{10}B and ^{11}B in gaseous boron fluoride has been demonstrated by mass-spectroscopic investigation [11, 12].

The surface tension of BF_3 in dyn/cm in the range from −116·4 to −92·6° can be found from the equation [13]:

$$\sigma = 20{\cdot}92 - 0{\cdot}22(t + 117{\cdot}0)$$

where t is the temperature in °C.

The parachor of BF_3: found 87·3, calculated for the electron configuration in which the boron atom is connected to the three fluorine atoms by the usual ordinary covalent links, 87·8 [13]. The heat of formation of boron fluoride from the elements is 273·5 kcal/mole; the latent heat of vaporization is 4·680 kcal/mole [6]. The heat capacity at 5° is 11·7 cal/mole [14].

Electron diffraction studies and Raman spectral data show that the BF_3 molecule has a planar structure with the boron atom in the centre

Table 3. Interatomic distances in molecules of some compounds of boron

Compound	Distance Å			
BF_3	B—F	1·30	F—F	2·25
BCl_3	B—Cl	1·73	Cl—Cl	2·99
BBr_3	B—Br	1·87	Br—Br	3·25
BI_3	B—I	2·08	—	
CH_3BF_2	B—F	1·30	B—C	1·60
$(CH_3)_2BF$	B—F	1·29	B—C	1·55
$(CH_3)_3B$	B—C	1·56	C—C	2·70
$(C_2H_5)_3B$	B—C	1·56	—	
$(CH_3O)_3B$	B—O	1·38	—	
B_2H_6	B—B	1·86	—	
$(CH_3BO)_3$	B—C	1·57	—	

of an equilateral triangle of fluorine atoms [15—21]. All three bonds between the fluorine and boron atoms are equivalent and homopolar. The valency angle of the boron atom is 120°, the distances between the fluorine atoms are 2·25 Å and the length of the boron—fluorine bond is 1·30 Å.

On comparing these distances with those given for other boron halides and alkyl- and alkoxy-derivatives given in Table 3, it is seen that the interatomic distances are least in boron fluoride; consequently the volume of its molecule will also be least.

Fluorine has the highest electronegativity, as is seen from the following values of the electronegativity of certain elements (in electron volts):

H — 2·1	N — 3·0	O — 3·5	F — 4·0
C — 2·5	P — 2·1	S — 2·5	Cl — 3·0
Si — 1·8	As — 2·0	Se — 2·4	Br — 2·8
			I — 2·5

This situation leads to the fact that the BF_3 molecule possesses a stronger electropolar character than the other halides of boron.

2. CHEMICAL PROPERTIES

The boron atom in the BF_3 molecule is trivalent with an electron sextet envelope. This makes it a strong electron acceptor, capable of combining with molecules containing atoms which can be electron donors (O, N, S).

On the other hand, the atoms are very densely packed in the boron fluoride molecule, it has a small volume and possesses high electropolar properties. Boron fluoride therefore has the remarkable property of easily combining with the most varied organic and inorganic compounds without any noticeable steric hindrance, forming coordination compounds. In such compounds the boron atom is tetravalent, negatively charged and has a tetrahedral valency configuration.

Boron fluoride is included among compounds which are chemically very active. All its reactions can be divided into two groups: reactions which proceed with decomposition of the molecule of boron fluoride, and reactions in which the molecule of boron fluoride enters as a whole into newly formed compounds without changing its composition.

Boron fluoride in normal conditions does not react with steel, and therefore it may be stored in steel cylinders. At a temperature of 25° it does not react with teflone or polytetrafluoroethylene [22]. There are indications that boron fluoride inhibits the corrosion of iron by 60—80 per cent sulphuric acid [23]. However, boron fluoride on heating reacts energetically with many elements and with inorganic and organic compounds.

With metallic potassium or sodium heated to redness boron fluoride forms elementary boron and the fluoride of the metal [24]:

$$BF_3 + 3K \rightarrow B + 3KF$$
$$BF_3 + 3Na \rightarrow B + 3NaF$$

As a result of introducing gaseous BF_3 into fused (not overheated) aluminium, on cooling there is obtained a metal which has a particularly fine-grained structure [25].

In small quantities BF_3 inhibits the oxidation of fused magnesium and its alloys in air [26, 27]. Thus, the introduction of only 0·2—2 per cent BF_3 inhibits the combustion of magnesium in air. The use of boron fluoride in the soldering of magnesium is evidently based on this [28].

Like other boron halides, BF_3 reacts with hydrogen over heated Na, Al, Mg or Zn with the formation of diborane [29]:

$$2BF_3 + 3H_2 + 2Al \rightarrow B_2H_6 + 2AlF_3$$

The reduction of BF_3 with hydrogen in a tungsten arc gives a small quantity of crystalline boron [30].

On reacting with aluminium chloride or bromide, non-volatile aluminium fluoride (m. p. 1040°) and boron chloride or the corresponding bromide are formed [31, 32]:

$$BF_3 + AlCl_3 \rightarrow BCl_3 + AlF_3$$
$$BF_3 + AlBr_3 \rightarrow BBr_3 + AlF_3$$

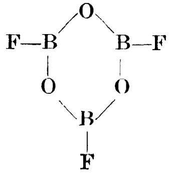
This reaction is used as a good method for the preparation of boron halides. To carry it out, boron fluoride is passed into a reaction vessel containing an aluminium halide, and the boron halide formed is distilled off from the reaction mixture. In the preparation of BCl_3 it is necessary to heat the reaction flask containing the $AlCl_3$ gradually over the naked flame of the burner. The yield of boron chloride is 80 per cent and of boron bromide 70 per cent. Boron chloride boils at 10°, and boron bromide at 91°.

Boron fluoride reacts with many metal oxides. With calcium hydroxide the reaction proceeds with the evolution of a considerable quantity of heat and with the formation of calcium borate and fluoroborate. This reaction can be used for the separation of boron fluoride from gases [33].

The carbonates of lithium, potassium, calcium and magnesium, potassium nitrate, SiO_2, $MgSiO_3$, $CaSiO_3$ and kaolin [34, 35] on reacting with BF_3 form boron oxyfluoride and the fluorides of the corresponding metals:

$3Li_2CO_3 + 9BF_3 \rightarrow (BOF)_3 + 6LiBF_4 + 3CO_2$
$3CaCO_3 + 3BF_3 \rightarrow (BOF)_3 + 3CaF_2 + 3CO_2$
$3K_2CO_3 + 9BF_3 \rightarrow (BOF)_3 + 6KBF_4 + 3CO_2$
$3MgCO_3 + 3BF_3 \rightarrow (BOF)_3 + 3MgF_2 + 3CO_2$
$6KNO_3 + 9BF_3 \rightarrow (BOF)_3 + 6KBF_4 + (6NO_2 + 1\frac{1}{2}O_2)$
$3KBO_2 + 6BF_3 \rightarrow 2(BOF)_3 + 3KBF_4$
$3MgO + 3BF_3 \rightarrow (BOF)_3 + 3MgF_2$
$3SiO_2 + 6BF_3 \rightarrow 2(BOF)_3 + 3SiF_4$
$MgSiO_3 + 3BF_3 \rightarrow (BOF)_3 + MgF_2 + SiF_4$
$3(Al_2O_3 . 2SiO_2) + 21BF_3 \rightarrow 7(BOF)_3 + 6AlF_3 + 6SiF_4$

Baumgarten [35] considers that the molecule of oxyfluoride has a cyclic structure:



Alumina and boron fluoride at a temperature of 450° form aluminium fluoride and boric anhydride [34]:

$$Al_2O_3 + 2BF_3 \rightarrow 2AlF_3 + B_2O_3$$

The reactions of BF_3 with kaolin and alumina can probably be used for the extraction of aluminium from silicate compounds.

With diborane, BF_3 gives an azeotropic mixture consisting of 41·6 per cent B_2H_6 and 58·4 per cent BF_3, boiling at −106° [36].

3. DERIVATIVES OF BORON FLUORIDE AND THEIR REACTIONS

Boron fluoride enters into chemical reactions with many organic substances.

When a gaseous mixture of boron fluoride and methyl chloride, in a ratio 2 : 1 by volume, is passed over granulated aluminium heated to 350°, trimethyl boron is formed as the main product [37].

Phenyllithium with boron fluoride ethyl etherate forms triphenyl boron [38].

A simple and convenient method for the synthetic preparation of trialkyl- and triaryl-derivatives of boron is the reaction of boron fluoride or its etherates, for example $BF_3 . O(C_2H_5)_2$, with organomagnesium halide compounds. This reaction may be represented by the equation [39]

$$BF_3 + 3RMgX \rightarrow B(R)_3 + 3MgFX$$

Triethyl boron [40], tri-*n*-propyl boron, tri*iso*propyl boron, tri*iso*butyl boron [41], tri*tert*butyl boron [42], tri*iso*amyl boron [41], tribenzyl boron [43, 44], tri*cyclo*hexyl boron [45], triphenyl boron [44, 46], tri-*p*-tolyl boron [47], tri-*p*-xylyl boron, tri-*p*-anisyl boron [43, 44], and tri-*α*-naphthyl boron [43, 48] have been obtained in good yield by this method. Some properties of these compounds are given in Table 4.

Table 4. Trialkyl- and triaryl derivatives of boron

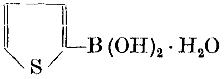
Name	Formula	m. p. (°C)	b. p. (°C/mm)	Yield (%)	Literature reference
Triethyl boron	$B(C_2H_5)_3$	—	90—96	80—85	[40]
Tri-*n*-propyl boron	$B(C_3H_7)_3$	—	156; 60/20	—	[41]
Tri*iso*propyl boron	$B[CH(CH_3)_2]_3$	—	33—35/12	—	[41]
Tri*iso*butyl boron	$B[CH_2CH(CH_3)_2]_3$	—	188; 86/20	—	[41]
Tri*tert*butyl boron	$B[C(CH_3)_3]_3$	—	71/12	—	[42]
Tri*iso*amyl boron	$B[CH_2CH_2CH(CH_3)_2]_3$	—	119/14	55	[41]
Tribenzyl boron	$B(CH_2C_6H_5)_3$	47	229—232/13	—	[43, 44]
Tri*cyclo*hexyl boron	$B(C_6H_{11})_3$	98—110	194/15	54	[45]
Triphenyl boron	$B(C_6H_5)_3$	136	203/15	50	[44]
Tri-*p*-tolyl boron	$B(C_6H_4CH_3)_3$	175	233—234/12	50	[47]
Tri-*p*-xylyl boron	$B[C_6H_3(CH_3)_2]_3$	146-7	221/12	—	[43]
Tri-*p*-anisyl boron	$B(C_6H_4OCH_3)_3$	128	—	—	[43, 44]
Tri-*α*-naphthyl boron	$B(C_{10}H_7)_3$	203	—	—	[43, 48]

This method is general for the preparation of trialkyl and triaryl derivatives of boron. The reaction is carried out in a solution of a Grignard reagent (20—40 per cent excess), to which is added BF_3 or $BF_3 . O(C_2H_5)_2$, and the mixture is heated and treated further in the appropriate manner. Since the trialkyl and triaryl compounds of boron are unstable and easily oxidized in air, they are usually separated by distillation in a current of dry nitrogen (they are liquids and capable of distillation) or they are precipitated with ammonia and the pure products are isolated by acidifying the ammoniates.

Preparation of triethyl boron [40]. Ethyl magnesium bromide, prepared from 70 g magnesium and 320 g ethyl bromide in 800 ml absolute ether, is placed in a two litre, three-necked flask fitted with a mechanical stirrer, a dropping funnel, a reflux condenser with nine bulbs and a gas inlet. The solution is heated on the water bath to gentle boiling (50°) and 105 g boron fluoride ethyl etherate (75 per cent of the theory) is added in the course of 1 hr with vigorous stirring. The temperature of the bath is brought to 80° and the mixture boiled for 2 hr with stirring. Then the ether and triethyl boron are distilled off into a dropping funnel in a current of nitrogen on the oil bath with a straight condenser. The dropping funnel is fitted to a Claisen flask. Then slowly, over 2—3 days, the ether is distilled off on the water bath and the triethyl boron is distilled at 90—96° in a current of nitrogen.

If an excess of boron fluoride is used, alkyl or aryl boric acids are obtained. Thus, if the Grignard reagent (prepared from 50 g C_6H_5Br in 200 ml ether), saturated with BF_3 (from 52 g KBF_4, 8 g B_2O_3 and 100 ml H_2SO_4), is boiled for 2 hr, after suitable treatment phenyl boric acid $C_6H_5B(OH)_2$ is obtained as snow-white, needle-shaped crystals [45].

From a Grignard reagent (prepared from 82 g α-bromothiophene in 150 ml ether) and BF_3 (from 30 g of a mixture of KBF_4 and B_2O_3 and 50 ml H_2SO_4), thienyl boric acid is formed as monohydrate with m. p. 134° [49]:



Boron fluoride reacts with methyl boric esters or the anhydrides of methyl and dimethyl boric acid with the formation of methyl boron fluorides [50]:

$$(CH_3O)_3B + 2BF_3 \rightarrow 3CH_3BF_2 + B_2O_3$$
$$3(CH_3)_2BOB(CH_3)_2 + 2BF_3 \rightarrow 6(CH_3)_2BF + B_2O_3$$

Methyl boron difluoride CH_3BF_2 is obtained in 95—98 per cent yield by reacting 30 ml $(CH_3O)_3B$ and 30 ml BF_3 [50]; it is a gaseous substance with m. p. $-130{\cdot}5°$, b. p. $-62{\cdot}3°/760$ mm, heat of vaporization 4750 cal/mole, and Trouton constant 22·6.

Dimethyl boron fluoride $(CH_3)_2BF$ is obtained in a yield of 81 per cent of the theoretical by condensing 65·5 ml dimethyl boric anhydride and 45·5 ml BF_3 [50]. M. p. $-147{\cdot}4°$; b. p. $-42{\cdot}2°$; heat of vaporization 5126 cal/mole; Trouton constant 22·2.

According to electron diffraction data the molecules of methyl boron difluoride and dimethyl boron fluoride have a planar structure, similar to BF_3 and $B(CH_3)_3$ [51]. The interatomic distances (Å) are:

	B—C	B—F
CH_3BF_2	$1{\cdot}60 \pm 0{\cdot}03$	$1{\cdot}30 \pm 0{\cdot}02$
$(CH_3)_2BF$	$1{\cdot}55 \pm 0{\cdot}02$	$1{\cdot}29 \pm 0{\cdot}02$

When boron fluoride reacts with the lower alcohols or with boroalkyl esters, alkoxy boron fluorides or mixed etherofluoroboric anhydrides of the general formulae $ROBF_2$ and $(RO)_2BF$ are obtained [52].

Methyl alcohol, when saturated with boron fluoride in the ratio of 1 : 1 and distilled with a fractionating column, gives methoxydifluoroboric anhydride CH_3OBF_2 of b. p. 87° (yield 10 per cent), boron fluoride methyl etherate $(CH_3)_2O\ .\ BF_3$ (yield 50 per cent) and a mixture of HF, HBF_4 and H_3BO_3 [52].

The action of boron fluoride on ethyl alcohol proceeds quantitatively according to the reaction [53]:

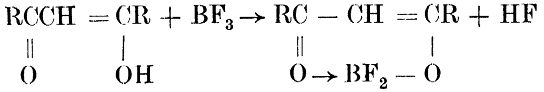
$$7BF_3 + 7C_2H_5OH \rightarrow C_2H_5OBF_2 + 3BF_3 \,.\, O(C_2H_5)_2 + 2HF + 2HBF_4 + H_3BO_3$$

The higher alcohols are decomposed by boron fluoride with the formation of hydrocarbon mixtures [54, 55].

Boromethyl ester $B(OCH_3)_3$, saturated with boron fluoride in the ratio of 2 : 1, is converted into the dimethoxyfluoranhydride of boric acid $(CH_3O)_2BF$, distilling at 53°. Boromethyl ester, saturated with boron fluoride in the ratio of 1 : 2, gives on distillation the methoxydifluoranhydride of boric acid CH_3OBF_2, which crystallizes at 41° [52]. It is immediately decomposed by the action of moisture.

Boroethyl ester $B(OC_2H_5)_3$ on distillation with BF_3 gives $C_2H_5OBF_2$ of b. p. 82° and m. p. 23° and $(C_2H_5O)_2BF$ of b. p. 78°.

β-Diketones in the enol form react with BF_3 splitting off HF [56]:



$$\underset{\underset{O}{\|}}{RC}CH=\underset{\underset{OH}{|}}{C}R + BF_3 \rightarrow \underset{\underset{O \rightarrow BF_2 - O}{\|\qquad\qquad |}}{RC - CH = CR} + HF$$

Acetoacetanilide $CH_3COCH_2CONHC_6H_5$ and BF_3 give a 79 per cent yield of difluoroboroacetoacetanilide $C_{10}H_{10}O_2NBF_2$ of m. p. 154–155°, which on hydrolysis with a dilute solution of $FeCl_3$ is converted into the original acetoacetanilide [57].

Amines and BF_3 in the presence of lithium are converted into the alkylamides of boric acid [58]. For example, ethylamine forms the triethylamide of boric acid according to the reaction

$$3C_2H_5NH_2 + BF_3 + 3Li \rightarrow B(NHC_2H_5)_3 + 3LiF + 1\tfrac{1}{2}H_2$$

Boron fluoride and acetyl fluoride [59, 60] form acetyl fluoroborate CH_3COBF_4 or $[CH_3CO]^+[BF_4]^-$. This compound may by the action of different reagents undergo the following transformations:

$$2CH_3COBF_4 + 2H_2O + K_2SO_4 \rightarrow 2CH_3COOH + H_2SO_4 + 2KBF_4$$

$$CH_3COBF_4 + NaF \rightarrow CH_3COF + NaBF_4$$

$$CH_3COBF_4 + KCl \xrightarrow[(CH_3CO)_2O]{BF_3 \cdot O(C_2H_5)_2} CH_3COCl + KBF_4$$

$$CH_3COBF_4 + NaNO_2 \rightarrow CH_3CONO_2 + NaBF_4$$

$$CH_3COBF_4 + CH_3COOH \rightarrow CH_3COF + CH_3COOH \,.\, BF_3$$

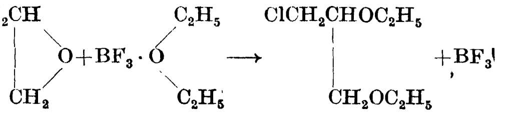
$$CH_3COBF_4 + (C_2H_5)_2O \rightarrow CH_3COF + BF_3 \,.\, O(C_2H_5)_2$$

$$CH_3COBF_4 + (C_2H_5)_2O \xrightarrow[100^\circ]{\text{in an autoclave}} C_2H_5F + CH_3COOC_2H_5 \,.\, BF_3$$

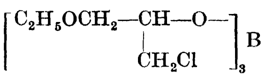
$$CH_3COBF_4 + C_6H_6 \rightarrow C_6H_5COCH_3 + HF + BF_3$$

Tertiary Oxonium Fluoroborates

Meerwein and collaborators [61—63] studied in detail the action of boron fluoride etherates on α-oxides and found that when epichlorhydrin is added dropwise to $BF_3 . O(C_2H_5)_2$ in excess of ether a reaction takes place with a large heat effect and the separation from the reaction mixture of a semi-solid mass which after some time changes into a colourless, crystalline substance. If such a reaction mixture is decomposed with water or soda solution without previously separating the crystals formed, there is obtained not γ-chloropropylene glycol diethyl ether which would be expected on the basis of the reaction



but 1-ethoxy-3-chloropropanol-2, $ClCH_2CH(OH)CH_2OC_2H_5$ in 72 per cent yield and ethyl alcohol in 64·4 per cent yield. An independent investigation of the ether solution and the separated crystals showed that the former contains as chief product the boron ester of 1-ethoxy-3-chloropropanol-2 of the structure

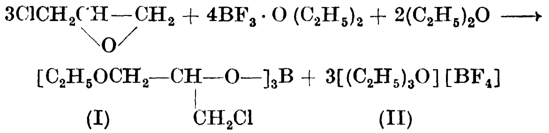


$$\left[\begin{array}{l}C_2H_5OCH_2\text{—}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}\text{—}O\text{—}\end{array}\right]_3 B$$

and a small quantity (10 per cent) of the boron fluoride compound of γ-chloropropylene glycol monoethyl ether

$$\begin{array}{r}ClCH_2CH(OH)CH_2OC_2H_5\\ |\\ BF_3\end{array}$$

The crystalline product proved to be triethyloxonium fluoroborate $[(C_2H_5)_3O]\,[BF_4]$. Thus, the reaction of epichlorydrin with boron fluoride ethyl etherate (in excess of ethyl ether) may be represented by the following equation:



$$3ClCH_2\underset{\diagdown O \diagup}{CH\text{—}CH_2} + 4BF_3\cdot O\,(C_2H_5)_2 + 2(C_2H_5)_2O \longrightarrow$$

$$\underset{(I)}{[C_2H_5OCH_2\text{—}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}\text{—}O\text{—}]_3B} + \underset{(II)}{3[(C_2H_5)_3O]\,[BF_4]}$$

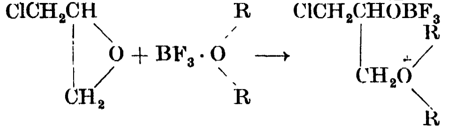
The yield of the boron ester of 1-ethoxy-3-chloropropanol-2 (I) is 74 per cent, and the yield of triethyloxonium fluoroborate (II) is 90 per cent of the theoretical. If, however, the reaction is carried out at a higher temperature, in that the epichlorohydrin is added to the $BF_3 . O(C_2H_5)_2$ in ethyl ether at such a rate that the ether boils constantly, and the mixture is stirred for 2 hr, triethyloxonium fluoroborate is obtained in a yield of 100 per cent.

The boron fluoride compound of dimethyl ether reacts with epichlorohydrin in a similar way. At a temperature of 35° the reaction proceeds extremely vigorously, the boron ester of 1-methoxy-3-chloropropanol-2 being formed in 87 per cent yield and trimethyloxonium fluoroborate in 98 per cent yield. Small amounts of the boron fluoride compound of γ-chloropropylene glycol monomethyl ether are also obtained.

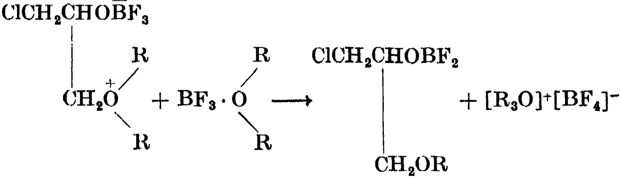
The boron fluoride compound of di-*n*-propyl ether with epichlorhydrin in excess of dipropyl ether, in the same conditions as with diethyl ether, gives tripropyloxonium fluoroborate with a yield of only 30 per cent [62]. Alkyl ethers of higher molecular weight do not form oxonium salts at all. Consequently the capacity of the ether oxygen to exhibit its high valency falls in proportion to the increase in size of the hydrocarbon radicals.

Meerwein [62] considers that the following mechanism is probable for the formation of oxonium salts:

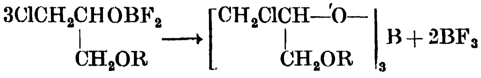
(I)



(II)



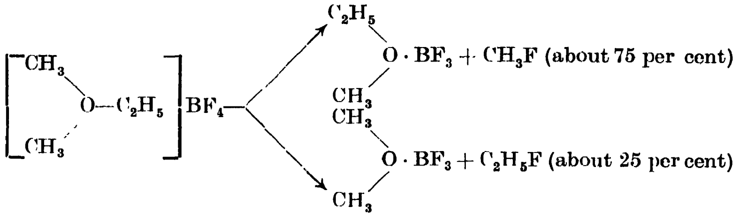
(III)



When boron fluoride etherates react with epichlorhydrin at low temperatures, inner betaine-like tertiary oxonium salts are first formed according to scheme (I). Then the salts formed react with a new molecule of boron fluoride etherate and form tertiary oxonium salts and the ether of 1-alkoxy-3-chloropropanol-2 with difluoroboric acid according to scheme (II). The latter compound is not isolated. It is considered very unstable and easily decomposes according to scheme (III).

The reaction of boron fluoride etherates with ethylene oxide and proceeds in a similar way.

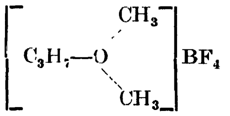
The tertiary oxonium fluoroborates are a new and very interesting class of organic compounds. They dissolve in nitromethane, nitrobenzene, acetone and methylene chloride, are thermally unstable and on dry distillation they almost quantitatively decompose into boron fluoride etherates and alkyl fluorides. For example, triethyloxonium fluoroborate on dry distillation splits into boron fluoride ethyl etherate with a yield of 92 per cent and ethyl fluoride with a yield of 67·4 per cent. Salts with alkyl radicals of unlike structure split in several ways. Thus, dimethylethyloxonium fluoroborate decomposes simultaneously in the following two ways:



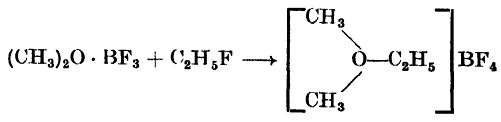
CH₃
O—C₂H₅
CH₃
BF₄
C₂H₅
O · BF₃ + CH₃F (about 75 per cent)
CH₃
CH₃
O · BF₃ + C₂H₅F (about 25 per cent)
CH₃

The thermal decomposition of oxonium fluoroborates in certain conditions is reversible, although the components on the right hand side of the equation combine again very slowly with the formation of trialkyloxonium fluoroborates.

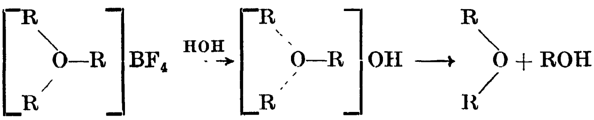
For example. $BF_3 . O(CH_3)_2$ (1·7 moles) and CH_3F (1 mole) on standing for three months in a sealed tube give trimethyloxonium fluoroborate in 38 per cent yield. After 4 months $BF_3 . O(C_2H_5)_2$ and CH_3F form methyldiethyloxonium fluoroborate in a yield of 52 per cent, but $BF_3 . O(CH_3)_2$ and C_3H_7F give only $[(CH_3)_3O]\ [BF_4]$ and do not form the expected



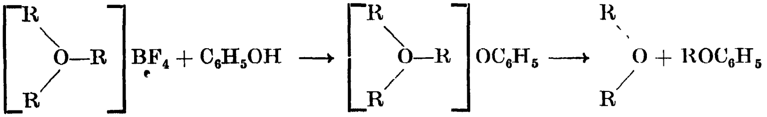
The addition of alkyl fluorides to boron fluoride etherates in excess of ether proceeds much more quickly. When 1 mole $BF_3 . O(C_2H_5)_2$, 1 mole C_2H_5F and 2 moles $O(C_2H_5)_2$ react in a sealed tube at room temperature for 3—4 weeks, crystalline $[(C_2H_5)_3O]\ [BF_4]$ begins to separate out. After 5 months the yield of this compound is 73 per cent. Ethyl fluoride combines still more quickly with $BF_3 . O(CH_3)_2$ to form dimethylethyloxonium fluoroborate according to the reaction



Trialkyloxonium fluoroborates are extremely reactive compounds. They react energetically with various organic compounds, easily transfer their alkyl radicals to them and are therefore often used as alkylating agents which are even more reactive than dialkyl sulphates. Water instantly hydrolyses them to oxonium compounds which are quickly converted into ethers and alcohols according to the reaction



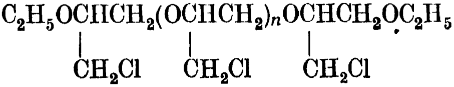
With alkyl ethers an exchange takes place in the alkyl groups. Alcohols and phenols are alkylated by trialkyloxonium fluoroborates with the formation of unstable intermediate trialkyloxonium alcoholates or phenolates respectively:



Phenols are easily alkylated in aqueous solutions of alkalis. Thus, free phenol and triethyloxonium fluoroborate form phenetole in 73 per cent yield, but sodium phenolate gives the same phenetole in 91 per cent yield. The α-ethyl ether of the γ-chlorhydrin of glycerin, on standing for 3 days with triethyloxonium fluoroborate gives γ-chloropropylene glycol diethyl ether in 55 per cent yield:

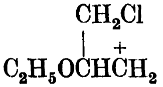
$$ClCH_2CH(OH)CH_2OC_2H_5 +$$
$$+ [(C_2H_5)_3O][BF_4] \rightarrow ClCH_2CH(OC_2H_5)CH_2OC_2H_5$$

Tertiary oxonium fluoroborates are used as catalysts in the addition of alkyl ethers to epichlorhydrin [63]. Epichlorhydrin and ethyl ether in the presence of triethyloxonium fluoroborate give linear polymers of the general formula

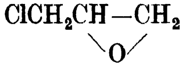


$$C_2H_5O\underset{\overset{|}{CH_2Cl}}{C}HCH_2(O\underset{\overset{|}{CH_2Cl}}{C}HCH_2)_nO\underset{\overset{|}{CH_2Cl}}{C}HCH_2OC_2H_5$$

in the composition of which, as is seen, there is one molecule of ethyl ether, "fixing" the ends of the chain. The extent of polymerization of the compounds formed depends on the quantities of $(C_2H_5)_2O$ and $[(C_2H_5)_3O][BF_4]$ used, the rate of addition of epichlorhydrin and the time of the reaction. The process takes place through the formation of ions principally of the following structure:

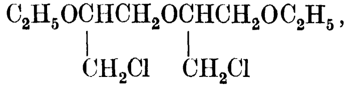


$$C_2H_5O\overset{\underset{|}{CH_2Cl}}{C}H\overset{+}{C}H_2$$

If 93 g  $ClCH_2CH{-}CH_2$ (epoxide, $\diagdown O \diagup$) are slowly added to a mixture of 8 g

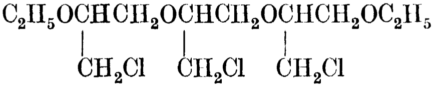
$[(C_2H_5)_3O]\ [BF_4]$ in 100 ml $(C_2H_5)_2O$ at 29°, and the mixture is heated to gentle boiling for 39 hr, then after appropriate treatment and distillation 6 g of the original epichlorhydrin, 27 g

$C_2H_5OCH(CH_2Cl)CH_2OC_2H_5$, 22 g



$$C_2H_5O\underset{CH_2Cl}{\underset{|}{CH}}CH_2O\underset{CH_2Cl}{\underset{|}{CH}}CH_2OC_2H_5,$$

14 g



$$C_2H_5O\underset{CH_2Cl}{\underset{|}{CH}}CH_2O\underset{CH_2Cl}{\underset{|}{CH}}CH_2O\underset{CH_2Cl}{\underset{|}{CH}}CH_2OC_2H_5$$

and 47 g of more complex compounds are obtained.

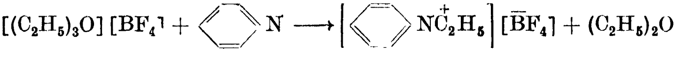
Organic acids react with triethyloxonium fluoroborate in such a way that the unstable oxonium salts of these acids are first formed and are converted into esters [61]:

$$[(C_2H_5)_3O]\ [BF_4]+RCOOH \rightarrow [(C_2H_5)_3O]OCOR \rightarrow (C_2H_5)_2O+C_2H_5OCOR$$

Esterification proceeds more easily in aqueous alkaline solutions: for example, by the action of triethyloxonium fluoroborate on free acetic acid ethyl acetate is formed with a yield of 46 per cent, but with an aqueous solution of sodium benzoate ethyl benzoate is obtained with a yield of 71 per cent. Dimethylethyloxonium fluoroborate with 3,5-dinitrobenzoic acid gives a mixture consisting of 70 per cent methyl dinitrobenzoate and 30 per cent ethyl dinitrobenzoate. Malonic and acetoacetic esters are alkylated by trialkyloxonium salts.

The reaction of trialkyloxonium fluoroborates with compounds containing nitrogen and sulphur proceeds in a similar manner. Ammonia and tertiary oxonium salts in the cold form a mixture of mono-, di- and trialkylamines. If 1·1 moles ammonia is used per 1 mole oxonium salt, secondary and tertiary alkylamines predominate in the mixture.

N-ethylpyridine fluoroboric acid is formed from triethyloxonium fluoroborate and pyridine according to the reaction



When this compound is heated, it is evidently possible to transfer the ethyl group into the nucleus and obtain ethyl pyridine by splitting off a molecule of fluoroboric acid.

The reaction of urea with triethyloxonium fluoroborate proceeds according to the equation

$$CO(NH_2)_2 + [(C_2H_5)_3O]\ [BF_4] \rightarrow [(NH_2)_2\overset{+}{C}OC_2H_5]\ [\overset{-}{B}F_4] + (C_2H_5)_2O$$

In a similar way trimethylamine oxide is ethylated by triethyloxonium fluoroborate, giving trimethylethoxyammonium fluoroborate $[(CH_3)_3\overset{+}{N}OC_2H_5][\overset{-}{B}F_4]$.

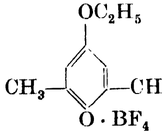
Diethyl sulphide and triethyloxonium fluoroborate give a quantitative yield of triethylsulphonium fluoroborate

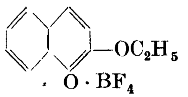
$$S(C_2H_5)_2 + [(C_2H_5)_3O][BF_4] \rightarrow [(C_2H_5)_3S][BF_4] + (C_2H_5)_2O$$

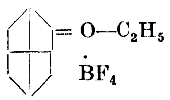
Acetamide and triethyloxonium fluoroborate give the very hygroscopic O-diethylacetimine fluoroborate $[CH_3\underset{\underset{NH}{\|}}{C}O(C_2H_5)_2][BF_4]$ [69], but diethyl sulphoxide forms diethylethoxysulphonium fluoroborate

$$[(C_2H_5)_2\overset{+}{S}OC_2H_5]\ [\overset{-}{B}F_4],$$

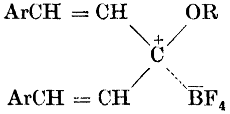
which quickly decomposes in air. Dimethylpyrone and coumarin with triethyloxonium fluoroborate form γ-ethoxy-α, α-dimethylpyrone fluoroborate (I) and α-ethoxybenzopyrone fluoroborate (II) respectively. Saturated ketones of the camphor type give addition compounds probably of the structure indicated by formula (III).

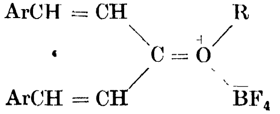

(I)


(II)


(III)

α,β-Unsaturated ketones of the dibenzalacetone type form intensely coloured salts with triethyloxonium fluoroborate, but it has not yet been established whether they are derivatives of carbonium (a) or oxonium (b):


(a)


(b)

Aryl Diazonium Fluoroborates

These compounds are usually prepared by the action of fluoroboric acid [64—72] or nitrosyl fluoroborate NO . BF_4 [73] on aryl diazonium salts.

For phenyl diazonium chloride the reaction may be represented by the equation

$$C_6H_5N_2Cl + HBF_4 \rightarrow C_6H_5N_2 . BF_4 + HCl$$

Aryldiazonium fluoroborates decompose easily and quantitatively on heating according to the reaction

$$ArN_2BF_4 \rightarrow ArF + BF_3 + N_2$$

The cleavage of aryldiazonium fluoroborates is an important method of introducing fluorine into different aromatic compounds. Scores of aromatic fluorine derivatives have been obtained in this way [74]. Some data about these compounds are given in Tables 5—10 [75].

Table 5. *Aryl fluorides from diazonium fluoroborates* [75]

Aryl fluoride (I)	Aryl diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield (%) II	Yield (%) I	b. p. or m. p. of (I) (°C)
Fluorobenzene	Phenyl-	122	70	80	b. p. 85
o-Fluorotoluene	*o*-Tolyl	106	82	90	b. p. 19 (17 mm)
m-Fluorotoluene	*m*-Tolyl-	108	76	87	b. p. 116
p-Fluorotoluene	*p*-Tolyl-	110	67	97	b. p. 117
4-Fluoro-1,3-xylene	2,4-Xylyl-	108	31	100	b. p. 143(749mm)
1-Fluoronaphthalene	1-Naphthyl-	113	91	98	b p. 80 (11 mm)
2-Fluoronaphthalene	2-Naphthyl-	108	90	69	m. p. 60
2-Fluorodiphenyl	2-Diphenylyl-	81	85	89	m. p. 60
3-Fluorodiphenyl	3-Diphenylyl-	91	85	50	m. p. 30
4-Fluorodiphenyl	4-Diphenylyl-	116	88	85	m. p. 75
Phenyl-1-fluoro-benzanthrone	Phenyl-1-benzanthronyl-	150	100	60	m. p. 195

Table 6. *Halogenoaryl fluorides from diazonium fluoroborates* [75]

Halogenoaryl fluoride (I)	Aryl diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield (%) II	Yield (%) I	b. p. or m. p. (I) (°C)
o-Difluorobenzene	*o*-Fluorophenyl-	150	45	30	b. p. 91—92 (751 mm)
p-Difluorobenzene	*p*-Fluorophenyl-	155	63	61	b. p. 88
1,2,4-Trifluorobenzene	2,4-Difluorophenyl-	145	42	17	b. p. 88
1,2,4-Trifluorobenzene	2,5-Difluorophenyl.	150	29	55	
o-Fluorobromobenzene	*o*-Bromophenyl-	132	40	55	b. p. 158 (756 mm)
m-Fluorobromobenzene	*m*-Bromophenyl-	141	86	78	b. p. 150 (764 mm)
p-Fluorobromobenzene	*p*-Bromophenyl-	133	64	75	b. p. 151 (746 mm)
o-Fluoroiodobenzene	*o*-Iodophenyl-	89	75	44	b. p. 73·6 (14 mm)
m-Fluoroiodobenzene	*m*-Iodophenyl-	105	98	68	b. p. 77·6 (19 mm)
2,5-Difluorotoluene	4-Fluoro-2-tolyl-	115	62	80	b. p. 117 (775 mm)
4-Fluoro-3-iodotoluene	2-Iodo-4-tolyl-	110	70	70	b. p. 122—125 (30 mm)
2,4-Difluoro-5-chloro-3-iodotoluene	3-Fluoro-6-chloro-2-iodo-4-tolyl-	218	65	85	b. p. 244—246
1-Fluoro-6-bromo-2,4-xylene	6-Bromo-2,4-xylyl-	161	60	100	b. p. 87—89 (11 mm)
4,6-Difluoro-5-iodo-1,3-dimethylbenzene	5-Fluoro-6-iodo-2,4-xylyl-	235	65	75	m. p. 42—43
1,4-Difluoronaphthalene	4-Fluoro-1-naphthyl-	137	47	66	m. p. 31·5
1-Fluoro-4-bromonaphthalene	4-Bromo-1-naphthyl-	152	97	66	m. p. 37
2-Fluoro-1-bromonaphthalene	1-Bromo-2-naphthyl-	99	23	23	m. p. 49
2,4,4′-Trifluorodiphenyl	4,4′-Difluoro-3-diphenylyl-	88	95	85	m. p. 83—84
2,4,4′,5-Tetra-fluorodiphenyl	2,4,4′-Trifluoro-5-diphenylyl-	102	83	90	m. p. 139
4,4′,6-Trifluoro-3,3′-ditolyl	4,4′-Difluoro3,3′-ditolyl-6-	94	52	52	b. p. 140 (12 mm)

The cleavage of aryldiazonium fluoroborates is also used for the preparation of pure boron fluoride, diluted only with nitrogen.

The cleavage of aryldiazonium fluoroborates often proceeds very energetically and it is therefore recommended that it be carried out in the presence of substances such as soda [76].

Table 7. *Aryl difluorides from bis-diazonium fluoroborates* [75]

Aryl difluoride (I)	Aryl bis-diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield (%) II	Yield (%) I	b. p. or m. p. (I) (°C)
m-Difluorobenzene	*m*-Phenylene-	206	88	44	b. p. 82—83 (752 mm)
p-Difluorobenzene	*p*-Phenylene-	186	82	33	b. p. 88
1,5-Difluoronaphthalene	1,5-Naphthalene-	180	92	54	m. p. 70·5
2,2′-Difluorodiphenyl	2,2′-Diphenylene	134	84	70	m. p. 117·5
3,3′-Difluorodiphenyl	3,3′-Diphenylene	106	98	50	b. p. 130 (14 mm)
4,4′-Difluorodiphenyl	4,4′Diphenylene-	138	95	85	m. p. 95
4,4′-Difluoro-3,3′ditolyl	3,3′-Ditolylene-4,4′-	127	60—70		m. p. 59

Table 8. *Fluoronitro compounds from diazonium fluoroborates* [75]

Fluoronitro compounds (I)	Aryl diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield (%) II	Yield (%) I	b. p. or m. p. (I) (°C)
o-Fluoronitrobenzene	*o*-Nitrophenyl-	135	74	18	b. p. 87 (11 mm)
m-Fluoronitrobenzene	*m*-Nitrophenyl-	178	79	53	b. p. 86 (19 mm)
p-Fluoronitrobenzene	*p*-Nitrophenyl-	156	96	47	b. p. 97 (28 mm)
2-Fluoro-3-nitrotoluene	6-Nitro-2-tolyl-	143	50	23	b. p. 110—111 (12 mm)
1-Fluoro-2,4-dimethyl-5-nitrobenzene	2,4-Dimethyl-5-nitrophenyl-	130	53	53	b. p. 133 (30 mm)
4,4′-Difluoro-2-nitrodiphenyl	2-Nitro-4,4′-diphenylene	128	95	10	m. p. 94·6
4,4′-Difluoro-6-nitro-3,3′-ditolyl	6-Nitro-3,3′-ditolylene	98	98	10	m. p. 89·5
2-Fluoro-5-chloro-4-nitrotoluene	4-Chloro-5-nitro-2-tolyl-	153	61	50	b. p. 247 (750 mm) m. p. 19
3,5-Dimethyl-2-fluoro-1-bromo-6-nitrobenzene	2,4-Dimethyl-6-bromo-5-nitrophenyl-	195	67	45	m. p. 51
p-Fluoro-N-dimethylaniline	*p*-Dimethylaminophenyl-	151	56	17	m. p. 35
p-Fluoro-N-diethylaniline	*p*-Diethylaminophenyl-	113	83	20	b. p. 92·5 (12 mm)

Table 9. *Fluoro-oxy compounds from diazonium fluoroborates* [75]

Fluoro compound (I)	Aryl diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield %		b. p. or m. p. (I) (°C)
			II	I	
o-Fluoroanisole	*o*-Anisyl-	125	52	67	b. p. 64 (17 mm)
m-Fluoroanisole	*m*-Anisyl-	68	100	69	b. p. 51 (15 mm)
p-Fluoroanisole	*p*-Anisyl-	139	85	67	b. p. 57 (19 mm)
2-Fluoro-4-bromo-anisole	2-Methoxy-5-bromophenyl-	156	92	54	m. p. 16
2-Fluoro-4-nitro-anisole	2-Methoxy-5-nitro-phenyl-	173	85	13	m. p. 104·6
3-Fluoro-2-cresol-methyl ether	2-Methoxy-3-tolyl-	88	68	62	b. p. 59 (19 mm)
3-Fluoro-3-cresol-methyl ether	2-Methoxy-5-tolyl-	122	82	48	b. p. 72 (12 mm)
1-Fluoro-2,4-dimethyl-6-bromo-5-methoxy-benzene	2,4-Dimethyl-6-bromo-5-methoxy-phenyl-	105	70	80	b. p. 125 (15 mm)
3-Fluoro-4-methoxy-diphenyl ether	2-Methoxy-5-phenoxyphenyl-	145	100	—	
o-Fluorophenetole	*o*-Ethoxyphenyl-	135	69	35	b. p. 64 (11 mm)
m-Fluorophenetole	*m*-Ethoxyphenyl-	70	75	47	b. p. 65 (15 mm)
p-Fluorophenetole	*p*-Ethoxyphenyl-	105	75	50	b. p. 71 (18 mm)
2-Fluoro-4-nitro-phenetole	2-Ethoxy-5-nitro-phenyl-	179	90	6	m. p. 77

Table 10. *Fluoro esters from ester diazonium fluoroborates* [75]

Fluoro ester (I)	Ester diazonium fluoroborate (II)	Decomp. temp. (II) (°C)	Yield (%)			b. p. of ester (°C)
			II	ester	acid	
Ethyl-*o*-fluorobenzoate	*o*-Carbethoxyphenyl-	106	90	87	45	102 (12 mm)
Ethyl-*p*-fluorobenzoate	*p*-Carbethoxyphenyl-	94	96	89	73	105 (25 mm)
Diethyl-4-fluoro-*o*-phthalate	3,4-Dicarbethoxy-phenyl-	125	98	50	—	165—170 (25 mm)

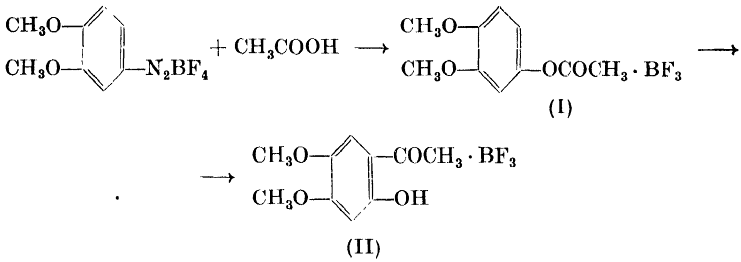
In a medium of glacial acetic acid phenyldiazonium fluoroborate splits with the formation of phenyl acetate in the form of a coordination compound with boron fluoride [77]:

$$C_6H_5N_2BF_4 + CH_3COOH \xrightarrow{\text{boiling}} C_6H_5OCOCH_3 \,.\, BF_3 + HF + N_2$$

After hydrolysis this compound may be isomerised to *p*-hydroxyacetophenone:

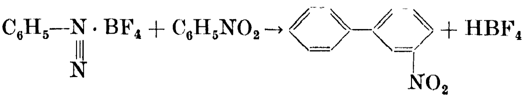
$$C_6H_5OCOCH_3 \rightarrow HOC_6H_4COCH_3,$$

On boiling 3,4-dimethoxyphenyldiazonium fluoroborate with glacial acetic acid, instead of forming the expected 3,4-dimethoxyphenyl acetate (I), it at once gives 3,4-dimethoxy-6-acetyl phenol (II) [78]:

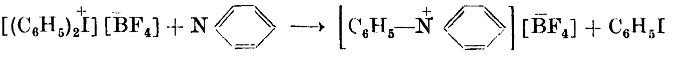


The investigations of A. N. Nesmeyanov and L. G. Makarova [79] on the thermal decomposition of phenyldiazonium fluoroborate in a medium of benzene derivatives containing *m*-orientating substituents are of great interest, and they showed that phenyldiazonium fluoroborate undergoes decomposition with the formation of a phenyl cation which enters into the *m*-position of the substituted benzene in question.

In nitrobenzene heterolytic decomposition takes place in such a way that the phenyl cation which is formed as a positively charged particle replaces the hydrogen of the nitrobenzene in the *m*-position according to the orientation rule, and forms *m*-nitrodiphenyl:



Diphenyliodonium fluoroborate undergoes the same heterolytic decomposition in a medium of pyridine with transfer of the phenyl in the form of a cation to the nitrogen atom of the pyridine ring and the formation of phenyl pyridinium fluoroborate [80]:



Phenylpyridinium fluoroborate was first obtained by A. N. Nesmeyanov and L. G. Makarova; a method of preparing it synthetically is described in the first section of *Syntheses of Organic Compounds* [81]. Tetraphenylphosphonium, tetraphenylarsonium, tetraphenylstibonium, triphenylsulphonium and triphenylselenonium fluoroborates were also prepared by this method [80].

A. N. Nesmeyanov and collaborators [82] used the method of decomposition of aryldiazonium fluoroborates for the preparation of certain organometallic compounds, for example tetraphenyl lead (decomposition of phenyldiazonium fluoroborate with metallic lead powder).

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CHAPTER III

COORDINATION COMPOUNDS OF BORON FLUORIDE

BORON fluoride forms coordination compounds with most varied inorganic and organic substances which contain elements capable of exhibiting their highest valency or carbon atoms with double and triple bonds. Such coordination compounds are usually prepared by saturating a specific substance with boron fluoride and are products formed by the reaction of whole molecules which do not undergo any appreciable changes of composition during the process of formation.

Many coordination compounds of boron fluoride possess high stability: the solids may be recrystallized from solvents, and the liquids converted to the vapour state and distilled without decomposition *in vacuo* or at atmospheric pressure. For example, boron fluoride ammoniate is recrystallized from water [1]; boron fluoride ethyl etherate distils at 124° at atmospheric pressure; the compound of boron fluoride and pyridine dissociates only at a temperature above 300° [2].

The great tendency of boron fluoride to complex formation depends upon its small molecular volume, high electro-polarity and the unsaturated character of the boron atom which favours coordination.

Although there is no single point of view on the nature of the forces which determine the formation of coordination compounds of boron fluoride, chemical as well as van der Waals' forces take part in their formation.

From the point of view of electron structure the formation of coordination compounds of boron fluoride may be described in this way: Organic and inorganic molecules having donor atoms with a free pair of electrons (O, N, S) give this pair of electrons to the boron acceptor atom. As a result the electron sextet envelope of boron is made up into an octet.

Between the boron fluoride and the molecule of another substance a donor—acceptor bond is formed, and in the newly formed compounds the boron atom becomes tetravalent and negatively charged.

The change of valency and number of bonds leads to a change from the planar configuration of the BF_3 molecule to a tetrahedral one, the three fluorine atoms and the donor atom (O, N, S) being at the apices of the tetrahedron, and the boron atom at the centre.

With substances capable of being found in the associated state (water, alcohols, acids), boron fluoride can form coordination compounds which may contain one, two or a larger number of associated molecules per mole of BF_3. With all other non-associated (amines, amides, acid anhydrides) or weakly associated (ethers, esters, ketones) compounds boron fluoride forms coordination compounds of mole for mole composition.

Boron fluoride coordination compounds are often formed as intermediate products in reactions in which BF_3 is used as a catalyst, and play an important part in the activation of boron fluoride.

Nobody now doubts the fact that the high catalytic activity of BF_3 depends upon its property of forming complexes with organic compounds which contain unsaturated carbon atoms or elements capable of displaying their higher valency [3].

In the formation of coordination compounds the increase of valency of the boron and donor atoms leads to a weakening of the remaining bonds existing in the boron and donor atoms, and to an increase in the interatomic distances. The organic molecules in these compounds are therefore activated, exist in an excited state and easily enter into different reactions.

Many boron fluoride coordination compounds surpass free BF_3 in their catalytic activity and are therefore used as specific independent catalysts. Sometimes these compounds serve simply as a convenient form of using BF_3 as a catalyst.

1. COORDINATION COMPOUNDS OF BORON FLUORIDE WITH INORGANIC SUBSTANCES

Coordination Compounds of BF_3 *with Inorganic Salts*

If a base is defined as a donor—"a substance which has a lone pair of electrons which may be used to complete the stable group of another atom," and an acid as an acceptor—"a substance which can employ a lone pair from another molecule in completing the stable group of one of its own atoms" [4], the boron fluoride may be considered a typical aprotonic acid. At the same time, as found by [5], BF_3 is a primary aprotonic acid, the neutralization of which by bases does not require energy of activation.

As a typical aprotonic acid BF_3 reacts with metal fluorides with the formation of stable fluoroborates of the general formula $MeBF_4$ or $MeF \cdot BF_3$. For example, by the action of boron fluoride on heated sodium fluoride sodium fluoroborate is obtained [6, 7]: $BF_3 + NaF \rightleftarrows NaBF_4$.

Salts of fluoroboric acid may also be prepared by neutralizing aqueous solutions of this acid with the corresponding bases or by dissolving metal oxides in the acid. On heating they again split off boron fluoride comparatively easily [7—10] and they are therefore often used as a basic raw material for its preparation, as described in the first chapter.

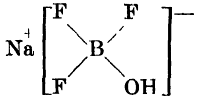
The heat of addition of boron fluoride to CsF, RbF and KF is about 30 kcal/mole [8]. The fluoroborates of these metals are only slightly soluble in water, whereas the sodium and lithium salts are readily soluble, and aqueous solutions of $LiBF_4$ have a strongly acid reaction. The Ca, Mg, Sr, Ba, Cu, Fe, Mn, Zn and Cd salts are very hygroscopic, easily soluble in water and are usually obtained as hydrated crystals with two, four or a larger number of molecules of water of crystallization [7, 10], for example $Ba(BF_4)_2 . 2H_2O$, $Zn(BF_4)_2 . 6H_2O$, $Mn(BF_4)_2 . 6H_2O$, $Cu(BF_4)_2 . 6H_2O$ and $Cd(BF_4)_2 . 6H_2O$. The Zn and Hg salts are obtained by dissolving the metals in HBF_4. The mercury salt has the composition $HgBF_4 . HF . H_2O$ and is easily soluble in water and in 80 per cent ethyl alcohol. The Fe, Co and Ni salts are not dehydrated over P_2O_5 and split off water only on heating.

The hexahydrates of Mg, Cu, Mn and other metals are considered [10] as aquosalts with coordination number 6 and the following formula; $[Me(H_2O)_6]\ [BF_4]_2$; for the strontium salt with coordination number 4 the formula $[Sr(H_2O)_4]\ [BF_4]_2$ has been proposed and for the silver salt the formula $[Ag(H_2O)]\ [BF_4]$.

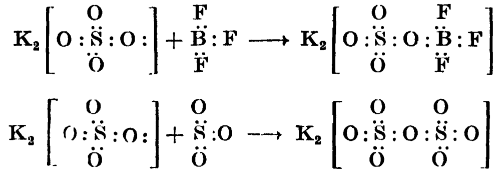
Many fluoroborates are capable of forming ammoniates, similar to the hydrates, for example, $[Ni(NH_3)_6]\ [BF_4]_2$, $[Zn(NH_3)_4]\ [BF_4]_2$, $[Ag(NH_3)_4]\ [BF_4]$ [10], $[Co(NH_3)_6]\ [BF_4]_3$, $[Cr(NH_3)_6]\ [BF_4]_3$ [9]. Being thermally unstable they easily and irreversibly decompose with the formation of metal fluorides, ammonia, ammonium fluoroborate and the sublimed ammoniate of boron fluoride. The decomposition of the cobalt salt may be represented thus:

$$3\ Co(NH_3)_6(BF_4)_3 \rightarrow 3\ CoF_2 + 6\ BF_3 . NH_3 + 3\ NH_4 . BF_4 + 8NH_3 + \tfrac{1}{2}\ N_2$$

Klinkenberg [11, 12] studied the crystalline structure of some fluoroborates and showed that salts such as $NaBF_4$, $CsBF_4$ and $TlBF_4$ are isomorphous with the corresponding perchlorates, for example, $KClO_4$. The substitution of a fluorine ion by a OH ion in fluoroborates does not disturb the lattice structure, and therefore the salt $BF_3 . NaOH$, which may formally be described as a reaction product of BF_3 and NaOH, is also isomorphous with $NaBF_4$ and may be considered as the sodium salt of monohydroxyfluoroboric acid of the following structure :



Boron fluoride $\underset{\ddot{F}}{F:B:F}$ is according to its structure analogous to sulphur trioxide $\underset{\ddot{O}}{O:S:O}$ and like the latter enters into an addition reaction with sulphates and phosphates in order to make up the electron sextet envelope of the boron atom to an octet [13—15]. For example, potassium sulphate forms a compound $BF_3 . K_2SO_4$, analogous to $SO_3 . K_2SO_4$ according to the reaction:

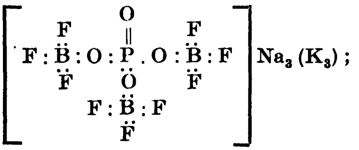


$$K_2\left[\begin{array}{c} O \\ O:\ddot{S}:O: \\ \ddot{O} \end{array}\right] + \begin{array}{c} F \\ \ddot{B}:F \\ \ddot{F} \end{array} \longrightarrow K_2\left[\begin{array}{c} O \quad\;\; F \\ O:\ddot{S}:O:\ddot{B}:F \\ \ddot{O} \quad\;\; \ddot{F} \end{array}\right]$$

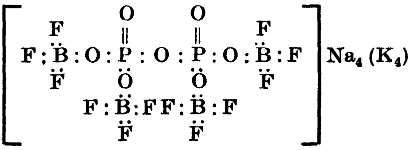
$$K_2\left[\begin{array}{c} O \\ O:\ddot{S}:O: \\ \ddot{O} \end{array}\right] + \begin{array}{c} O \\ \ddot{S}:O \\ \ddot{O} \end{array} \longrightarrow K_2\left[\begin{array}{c} O \quad\;\; O \\ O:\ddot{S}:O:\ddot{S}:O \\ \ddot{O} \quad\;\; \ddot{O} \end{array}\right]$$

However, the rate of formation of these two compounds is different. Whereas SO_3 adds on to finely powdered potassium sulphate with the formation of $SO_3 . K_2SO_4$ ($K_2S_2O_7$) at room temperature, the addition of one molecule of BF_3 takes place only when a stream of boron fluoride is passed over potassium sulphate heated to a temperature of 250—300°. The product on cooling is a white, crystalline mass which melts at 240°, and at 270° bubbles and decomposes. The product is comparatively readily soluble in water, but does not dissolve in other solvents.

Numerous coordination compounds of boron fluoride of different composition have also been obtained with different sulphates, phosphates and pyrophosphates. For example, $Na_2SO_4 . BF_3$, $Co_2SO_4 . 2BF_3$, $FeSO_4 . BF_3$, $Na_3PO_4 . 3BF_3$, $K_3PO_4 . 3BF_3$, $Na_4P_2O_7 . 4BF_3$, $K_4P_2O_7 . 4BF_3$ [14]. It was found that, as in the reactions with sulphur trioxide, the reaction of boron fluoride with alkali sulphates proceeds more easily the higher the atomic weight of the metal. Thus, lithium sulphate absorbs only about 0·1 mole BF_3, but caesium sulphate adds two molecules of BF_3. The sulphates of the alkaline earth metals, according to the data of Baumgarten [14], do not add boron fluoride at all. Sodium and potassium phosphate and pyrophosphate add three and four molecules of BF_3 respectively and form compounds of the composition shown. The structure of such compounds may, by analogy with the addition products of BF_3 to sulphates, be represented by the following formulae:



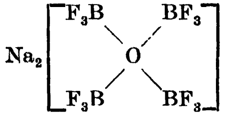
$$\left[\begin{array}{c} F \qquad \overset{O}{\|} \qquad F \\ F:\ddot{B}:O:\dot{P}.O:\ddot{B}:F \\ \ddot{F} \qquad \ddot{O} \qquad \ddot{F} \\ F:\ddot{B}:F \\ \ddot{F} \end{array}\right] Na_3(K_3);$$



$$\left[\begin{array}{c} F \qquad \overset{O}{\|} \qquad \overset{O}{\|} \qquad F \\ F:\ddot{B}:O:\dot{P}:O:\dot{P}:O:\ddot{B}:F \\ \ddot{F} \qquad \ddot{O} \qquad \ddot{O} \qquad \ddot{F} \\ F:\ddot{B}:F\,F:\ddot{B}:F \\ \ddot{F} \qquad \ddot{F} \end{array}\right] Na_4(K_4)$$

All these coordination compounds are stable and split off BF_3 only at temperatures above 300°. They dissolve in water, but undergo complete hydrolysis to their initial components only if the aqueous solutions are boiled and allowed to stand for a long time. These compounds, like the complex with potassium sulphate, are prepared by passing a stream of gaseous BF_3 over the salts in the form of fine powder at a temperature of 240—400°. Their formation is accompanied by caking of the salts and proceeds very slowly, because the main reaction takes place essentially on the surface between the solid and the gas phases.

The following structure is ascribed to BF_3 coordination compounds of the $Na_2O\,.\,4BF_3$ type [16];



This compound is the basic raw material for the manufacture of boron fluoride in industry. In it, as is seen from the formula, an oxygen atom is the central atom of the coordination complex.

Coordination Compounds of BF_3 *with Water*

Boron fluoride combines with water very readily. Thus, 1 g water at 0° and 762 mm pressure absorbs 3·220 g BF_3, which is equivalent to an absorption of 1057 ml gaseous boron fluoride in 1 ml water [17]. The process of solution is accompanied by the evolution of 24·5 kcal/mole. At the same time different coordination and chemical compounds are formed depending on the amount of water:

$$\begin{aligned}
BF_3 + H_2O &\rightarrow BF_3\,.\,H_2O \quad \text{or } (HOBF_3)^- \, H^+ \\
BF_3 + 2\,H_2O &\rightarrow BF_3\,.\,2H_2O \quad \text{or } (HOBF_3)^- \, (H_3O)^+ \\
2\,BF_3 + 3\,H_2O &\rightarrow HBF_4 + B(OH)_3 + 2\,HF \\
4\,BF_3 + 3\,H_2O &\rightarrow 3\,HBF_4 + B(OH)_3
\end{aligned}$$

The last two reactions occur in dilute aqueous solutions of BF_3.

The first investigations of the reaction of boron fluoride with water may be traced back to the beginning of the last century [18]. Gay-Lussac and Thénard (1809), Davy (1812) and Berzelius (1845) considered that water dissolved BF_3 at room temperature with the formation of a quite definite compound—hydroxyfluoroboric acid, which is an oil that fumes strongly in air, of specific gravity 1·770, acting energetically on metals and oxides. On boiling, this oil loses about one-fifth part of the absorbed BF_3, after which it distils at 100°.

Basarow (1874) [17] fractionated an aqueous solution of boron fluoride and showed that the products distil at different temperatures, and the separate fractions have different specific gravities, and consequently do not represent an individual substance—fluoroboric acid. Gasselin (1892) [19] also obtained results disproving the formation of fluoroboric acid when BF_3 reacts with water.

Summarizing all these investigations, D. I. Mendeleev [20] came to the conclusion that "the behaviour of BF_3 towards water should be understood as a reversible reaction, because boron fluoride and water should, and do, give HF and $B(OH)_3$, but these by a reverse reaction give back BF_3 and water. Between these four substances and two reversible reactions an equilibrium sets in which is evidently dependent on the mass of the water. When BF_3 is present in a large excess, the equilibrium system which is capable of distillation (sp. gr. of the liquid 1·77) has the composition $BF_3 . 2H_2O$. It also forms corresponding salts. This is a corrosive liquid which has the properties of a strong acid but it has no action on glass, showing that there is no free HF produced. Under the action of water this system changes with the formation of boric acid and fluoroboric acid (HBF_4) according to the equation

$$4\ BF_3 . 2H_2O \rightarrow 3\ HBF_4 + B(OH)_3 + 5\ H_2O$$

Corresponding to this fluoroboric acid are its salts, for example, KBF_4. On evaporation of the aqueous solution fluoroboric acid decomposes with the liberation of hydrofluoric acid and the particular system is again obtained

$$2\ HBF_4 + 5\ H_2O \rightarrow B_2F_6H_{10}O_5 + 2\ HF$$

The compound of BF_3 with water is again included in the resulting solution which contains $(2BF_3) . 5H_2O$ (sp. gr. 1·58), identical with that formed when a solution of B_2O_3 in hydrofluoric acid is evaporated. Probably various other more or less stable equilibria and definite compounds between BF_3, HF and H_2O are possible."

In this way D. I. Mendeleev first expressed the idea that BF_3 and water, depending on the quantity of the latter, form different coordination compounds (hydrates) which possess definite properties and are capable of distillation. This important prediction was completely confirmed by later investigations. Thus, Meerwein and collaborators [21, 22] found that if 1 mole BF_3 is introduced into 2 moles water, boron fluoride dihydrate $BF_3 . 2H_2O$ is obtained. The product decomposes on distillation at ordinary pressure. It distils *in vacuo* without decomposition at 58·5—60° (1·2 mm), is a colourless liquid of $d_4^{20} = 1·623$, possesses strongly acid properties, and dissolves metals, their oxides and carbonates.

This hydrate adds to olefines, for example to propylene, according to the reaction

$$2CH_3CH = CH_2 + BF_3 . 2H_2O \rightarrow BF_3 . 2CH_3CH(OH)CH_3$$

Diazoacetic ester decomposes with explosion in the presence of $BF_3 . 2H_2O$. The dihydrate forms oxonium salts with certain organic compounds which contain oxygen. For example, with dioxane it gives a compound $BF_3 . 2H_2O . C_4H_8O_2$ with m. p. 142°, and with cineole a compound $BF_3 . 2H_2O . 2C_{20}H_{18}O_2$ with m. p. 59·5—61°. This dihydrate of boron fluoride is obtained by the fractional distillation of a solution of boric acid in concentrated hydrofluoric acid in a high vacuum.

On introducing BF_3 into liquid boron fluoride dihydrate in the cold the monohydrate $BF_3 . H_2O$, a colourless liquid of sp. gr. d_4^{15} 1·777, is obtained. Like the dihydrate it is strongly acid and forms salts with cineole and dioxane, and dissolves cellulose in the cold.

On passing 1 mole BF_3 into 2 moles water cooled in ice, McGrath and collaborators [23] obtained boron fluoride dihydrate of m. p. 5·9—6·1°. The product was a colourless liquid which did not fume in air and had no action on glass. When it was distilled in a heavy-duty column at a pressure from 1 to 100 mm it was found that boron fluoride dihydrate distilled completely within a range of 1—2° only under a pressure lower than 10 mm. At higher pressure a series of fractions of gradually decreasing specific gravity was obtained. At a pressure of 25 mm two fractions, of b. p. 85 and 93·5°, were separated. The first had d_4^{20} 1·6788, n_D^{20} 1·3411 and corresponded to the dihydroxyfluoroboric acid $[(HO)_2BF_2]H$ obtained by Nieuwland and collaborators [24] by the action of boron fluoride on water. It is considered probable that its formation is a result of the decomposition of boron fluoride dihydrate on distillation according to the reaction

$$3BF_3 . 2H_2O \rightarrow H_3BO_2F_2 + HF . 2BF_3 . 4H_2O$$

The second, higher boiling fraction is probably a mixture of different products from which the specific compounds of the repeated distillation are not separated.

Aqueous solutions of boron fluoride have been studied in detail in recent years [25—27].

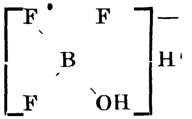
On a basis of the character of the Debyegram of boron fluoride dihydrate, taken at −60°, Klinkenberg and collaborators [28] established the isomorphism of fluoroborates and chlorates and demonstrated their close analogy with boron fluoride dihydrate. Data about the rhombic elementary nuclei of boron fluoride dihydrate and some fluoroborates are given in Table 11.

Table 11. *Crystalline structure of boron fluoride dihydrate and the fluoroborates of the alkali metals*

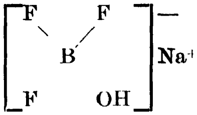
Salt	Axes of nucleus, Å			Axial ratios a : b : c	Literature reference
	a	b	c		
$BF_3 . 2H_2O$	8·74 ± 0·06	5·64 ± 0·03	7·30 ± 0·10	1·55 : 1 : 1·30	[28]
NH_4BF_4	8·89 ± 0·05	5·68 ± 0·05	7·21 ± 0·03	1·58 : 1 : 1·27	[28]
	9·06	5·64	7·23	1·606 : 1 : 1·262	[29]
$RbBF_4$	9·07	5·60	7·23	1·620 : 1 : 1·292	[29]
$CsBF_4$	9·43 ± 0·10	5·83 ± 0·07	7·65 ± 0·02	1·617 : 1 : 1·310	[7]
KBF_4	7·84	5·68	7·37	1·382 : 1 : 1·297	[30]
$NaBF_4$	6·25 ± 0·02	6·77 ± 0·02	6·82 ± 0·01	0·922 : 1 : 1·007	[7]
$NaOH . BF_3$	6·24 ± 0·02	6·82 ± 0·01	6·85 ± 0·01	0·915 : 1 : 1·004	[7]

By analogy with the isomorphism between NH_4ClO_4 and $HClO_4 . 2H_2O$ and by understanding the structure of the latter as a hydroxonium compound of formula $[H_3O] [ClO_4]$, Klinkenberg considers that $BF_3 . 2H_2O$ is also the hydroxonium salt of monohydroxyfluoroboric acid $[HOBF_3]H$, to which must correspond the formula $[H_3O] [HOBF_3]$.

Therefore by dissolving 1 mole BF_3 in 1 mole water, boron fluoride monohydrate is formed. In structure it is monohydroxyfluoroboric acid



Sodium monohydroxyfluoroborate of the structure



is a typical salt of a monohydrate.

Boron fluoride monohydrate is a strong acid and, like perchloric acid, is capable of adding yet another molecule of water and gives boron fluoride dihydrate of the structure $[H_3O]^+ [HOBF_3]^-$.

Coordination Compounds of BF_3 *with Hydrogen Sulphide*

Boron fluoride can form coordination compounds of different composition with hydrogen sulphide, as with H_2O, but they are all very unstable and exist only at low temperatures. By the method of thermal analysis (Fig. 1), the existence of an unstable and easily dissociated compound of composition $BF_3 . H_2S$ [31, 32] was demonstrated. On a basis of the character of the thermogram obtained the existence of a crystalline compound $BF_3 . 7H_2S$ is considered probable.

Coordination Compounds of BF_3 *with Inorganic Acids*

Boron fluoride is capable of forming coordination compounds with all inorganic acids which contain oxygen on account of the pair of electrons of the oxygen atom:

$$BF_3 + H_2SO_4 \rightleftarrows (HO)_2\overset{+}{S}O_2 : \overset{-}{B}F_3 \rightleftarrows \overset{+}{H} + BF_3 \,.\, HSO_4$$

$$BF_3 + H_3PO_4 \rightleftarrows (HO)_3P\overset{+}{O} : BF_3 \rightleftarrows \overset{+}{H} + BF_3 \,.\, H_2PO_4$$

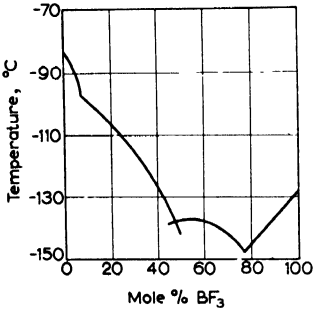


Fig. 1. The system H_2S—BF_3. Temp. °C; mole % BF_3.

The stability of these compounds is in direct relation to the strength of the acids: the stronger the acid, the less stable is the coordination compound of such acid with boron fluoride. The acid properties of these compounds are sharply reinforced in comparison with the original acids. In connection with this it is interesting to note that the electrical conductivity of a series of coordination compounds of boron fluoride was determined by the authors of the present monograph [33], and it was shown that the conductivity of the compounds with acids was lower than the conductivity of the acids. The conductivity increases with rise of temperature, as seen from Table 12.

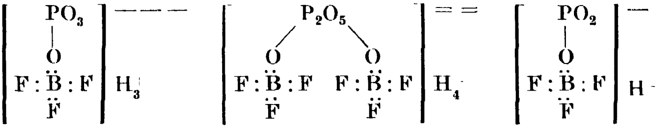
Table 12. Electrical conductivity of boron fluoride compounds at different temperatures

Temperature (°C)	Specific conductivity (ohm^{-1} cm^{-1})			
	H_2SO_4 (100·1%)	BF_3 . H_2SO_4	H_3PO_4	BF_3 . H_3PO_4
0	—	—	—	0·003257
5	0·022005	0·017147	—	0·004357
10	0·020177	0·020119	—	0·004600
15	—	0·025290	—	0·005209
20	0·033685	0·027058	—	0·005834
25	0·043595	0·035694	0·0510	0·007227
30	0·049742	0·041639	—	0·008148

Particularly interesting and important in practice are the coordination compounds of boron fluoride with phosphoric acids, which are widely used as catalysts in alkylation, polymerization and other reactions.

Solutions of phosphoric acids saturated with boron fluoride have been proposed as catalysts [34 –41].

In 1945 Academicians A. V. Topchiev and Ya. M. Paushkin [42–44] first found that on passing boron fluoride into phosphoric acids, not simply solutions but definite coordination compounds of the following composition are formed: for orthophosphoric acid $BF_3 . H_3PO_4$, for pyrophosphoric acid $H_4P_2O_7 . 2BF_3$ and for metaphosphoric acid $BF_3 . HPO_3$. They are all liquids, comparatively stable on keeping and are not decomposed on heating to 100°. Their structure may be represented thus:



The compound $H_3PO_4 . BF_3$ has $d_4^{20} = 1{\cdot}903$ and contains 41 per cent BF_3.

One volume of concentrated H_2SO_4 of sp. gr. 1·85 absorbs 0·5 volume BF_3 and forms a viscous, fuming liquid which is more volatile than sulphuric acid and which on mixing with water gives a dense, white precipitate [18, 45]. With nitric acid boron fluoride forms a compound $BF_3 . HNO_3$ [46]. Boric acid forms a coordination compound with boron fluoride. The indication by Nieuwland and collaborators [24, 47–49] that on passing an excess of BF_3 over solid orthoboric acid, dihydroxyfluoroboric acid is obtained in quantitative yield according to the reaction:

$$2BF_3 + 4H_3BO_3 \rightarrow [(HO)_2BF_2]H + 4HBO_2 + 2HF$$

should be regarded as very doubtful. The products on the right hand side of this equation are probably the result of the cleavage of the coordination compound of boron fluoride and boric acid. There is no doubt that even when boron fluoride is passed into water to an increase in weight corresponding to a ratio of 1 : 2, it is not dihydroxyfluoroboric acid which is obtained

$$2BF_3 + 4H_2O \rightarrow 2[(HO)_2BF_2]^-H^+$$

as the above authors think, but boron fluoride dihydrate, which on distillation at atmospheric pressure is split into dihydroxyfluoroboric acid and other compounds according to the reaction

$$3BF_3 . 2H_2O \rightarrow [(HO)_2BF_2]^-H^+ + HF . 2BF_3 . 4H_2O$$

Investigation of the solubility of BF_3 in liquid HF does not indicate the formation of coordination compounds, but the rapid increase in the solubility of BF_3 in HF with decrease in temperature (Table 13) gives a basis for assuming the possibility of the formation of an unstable coordination compound [50].

Table 13. *Solubility of boron fluoride in liquid hydrogen fluoride* [50]

Temperature (°C)	Pressure (atm)	Solubility (mole %)	Temperature (°C)	Pressure (atm)	Solubility (mole %)
—79	1·029	7·46	4·4	4·2	2·25
—43	1·029	4·36	4·4	8·4	4·20
—31	1·029	3·76	4·4	12·6	6·18
—26	1·029	3·29	20·5	4·2	1·92
4·4	1·029	0·61	20·5	8·4	3·25
20·5	1·029	0·51	20·6	12·6	4·77
43·3	1·029	0·34	43·3	4·2	1·18
—	—	—	43·3	8·4	2·40
—	—	—	43·3	12·6	3·22

Numerous facts about the promotion of the catalytic action of boron fluoride by hydrogen fluoride indicate that when they react fluoroboric acid is formed

$$BF_3 + HF \rightleftarrows HBF_4 \rightleftarrows H^+ + \overline{BF_4}$$

Fluoroboric acid may be regarded as an addition product of hydrogen fluoride to boron fluoride. It is not known in the free state, but its aqueous solutions and the salts described above exist.

The mixing of boron fluoride hydrate with hydrogen fluoride is accompanied by a vigorous exothermic reaction and the formation of the complex $H_2O \,.\, BF_3 \,.\, HF$ [51]. This complex may be regarded as the hydrate of fluoroboric acid as or an independent coordination compound; more probably the latter, because hydrates of acids are not very active catalytically, but the complex $H_2O \,.\, BF_3HF$ possesses extremely high activity. The formation of the following acid may be expected:

$$H_2O \,.\, BF_3 + HF \rightarrow H_2O \,.\, BF_3HF \rightarrow (BF_4 \,.\, H_2O)^- H^+ \text{ or } [BF_4]^- [H_3O]^+$$

The complex $H_2O \,.\, BF_3 \,.\, HF$ hardly corrodes glass, which serves as evidence of the absence of free hydrogen fluoride in it [51].

Wiberg and collaborators [52] point out that boron fluoride and hydrogen chloride form an unstable liquid component of composition $BF_3 \,.\, 3HCl$, which easily decomposes into the original molecules in the vapour. On studying the system BF_3—HCl by the method of thermal analysis (Fig. 2) Booth and Martin [53] did not observe any coordination compounds, which they explained as the incapability of the chlorine atom to act as a donor in relation to the boron atom. No coordination compound could be observed in the study of the system BF_3—HBr (Fig. 3) [54].

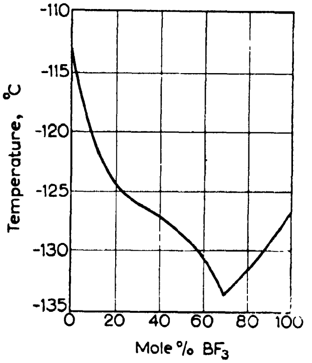


Fig. 2. The system BF_3—HCl. Temp. °C; mole % BF_3.

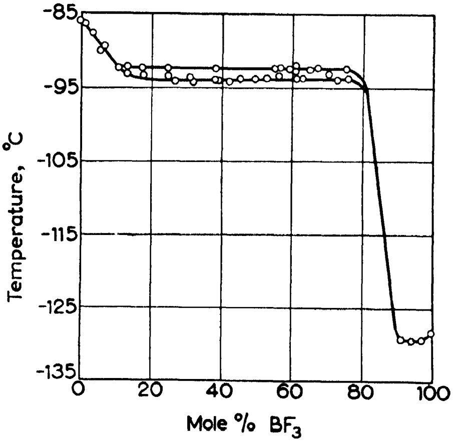


Fig. 3. The system BF_3—HBr. Temp. °C; mole % BF_3.

Coordination Compounds of BF_3 with Anhydrides and Halogenoanhydrides of Inorganic Acids

Attempts to establish the existence of coordination compounds of boron fluoride with the anhydrides of strong mineral acids by physico-chemical analysis lead to positive results not in all cases.

Boric anhydride and boron fluoride form coordination compounds $BF_3 . 2B_2O_3$ and $BF_3 . 3B_2O_3$ [55].

Phosphorus pentoxide and BF_3 form coordination compounds at low temperatures. On passing BF_3 over P_2O_5 for 1 hr at room or higher temperatures, addition products are not formed. At a temperature of 200° phosphorus pentoxide begins to sublimate in the stream of boron fluoride at the same rate as in the stream of hydrogen [56].

Iodic anhydride I_2O_5 does not react with BF_3 at temperatures from 20° to the decomposition of the anhydride [56]. No reaction is observed with BF_3 even with iodine when it is converted into vapour.

Sulphur dioxide and BF_3 give a coordination compound $BF_3 . SO_2$, which is unstable and easily dissociates above its melting point [53]. The latter is confirmed by the flat maximum on the freezing curve (Fig. 4).

On studying the system BF_3—NO_2 by the method of thermal analysis no definite compounds could be detected [53].

When the systems BF_3—PF_3 (Fig. 7), BF_3—POF_3 (Fig. 5), BF_3—$POCl_3$ and BF_3—PSF_3 were studied by the method of thermal analysis, in no case could definite compounds [57, 58] be detected. On passing BF_3 into PCl_3 at a temperature of —12° and below, an addition product $BF_3 . PCl_3$ which forms needle-shaped crystals is obtained; at —6° it begins to dissociate, in air it easily liberates all the BF_3 and pure PCl_3 remains in the residue [56].

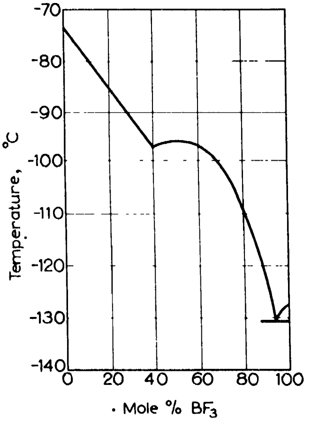


Fig. 4. The system BF_3—SO_2. Temp. °C; mole % BF_3.

Investigation of the system BF_3—SO_2F_2 by the method of thermal analysis shows the existence of a compound $BF_3 . SO_2F_2$ with m. p. —140·8° [57] (Fig. 6).

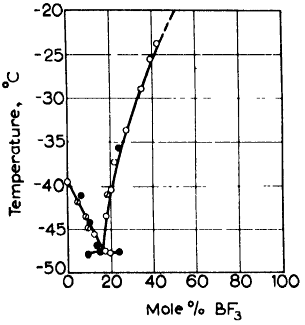


Fig. 5 The system BF_3—POF_3. Temp. °C; mole % BF_3.

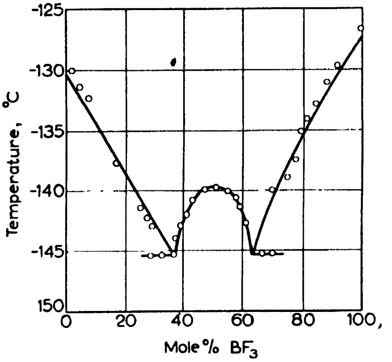


Fig. 6. The system BF_3—SO_2F_2. Temp. °C; mole % BF_3.

Coordination Compounds of BF_3 *with Phosphine*

There is contradictory information about the existence of coordination compounds of boron fluoride and phosphine. Besson [59] found that phosphine and BF_3 at a temperature of —50° or lower form a coordination compound $PH_3 \, . \, 2BF_3$. Wiberg and Heubaum [60] doubted the possibility of the existence of such a compound because the trivalent phosphorus atom in PH_3 possesses only one lone pair of electrons which it can give to the boron atom of one molecule of BF_3 in order to make the electron sextet envelope of boron up to an octet. For this purpose they repeated the work of Besson and found that at a temperature of —130° which excluded the possibility of the decomposition of the coordination compounds formed, on the action of excess BF_3 only one molecule of it was absorbed by one molecule of PH_3 and a compound $PH_3 \, . \, BF_3$ was obtained. As regards the product $PH_3 \, . \, 2BF_3$, in the author's opinion it is a derivative of phosphoric acid fluoroborate, which may be formed as a result of a secondary reaction according to the scheme

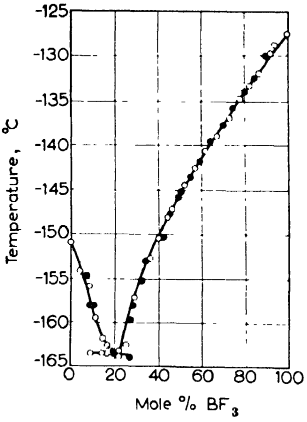


Fig. 7. The system PH_3 - BF_3. Temp. °C; mole % BF_3.

$$PH_3 \, . \, BF_3 \xrightarrow{-HF} PH_2(BF_2) \xrightarrow{+HF} [PH_3(BF_2)]\,F \xrightarrow{BF_3} [PH_3(BF_2)]\,[BF_4]$$

Later data of Martin and collaborators [54, 61], however, confirm that BF_3 and PH_3 at a temperature of —50° form two coordination compounds $PH_3 \, . \, BF_3$ and $PH_3 \, . \, 2BF_3$, which exist in the solid state. AsH_3 does not form definite coordination compounds with BF_3 [54].

Coordination Compounds of BF_3 *with Ammonia*

Boron fluoride and ammonia react very vigorously and form a coordination compound $BF_3 . NH_3$.

In laboratory practice it is usually obtained by passing ammonia through organic substances containing combined or uncombined boron fluoride [62, 63], for example:

$$BF_3 . O(C_2H_5)_2 + NH_3 \rightarrow BF_3 . NH_3 + (C_2H_5)_2O$$

Boron fluoride ammoniate $BF_3 . NH_3$ is a white, opaque, solid substance of m. p. 163° (in a rapid determination) and d_4^{25} 1·864 [64]. The heat of formation of solid $BF_3 . NH_3$ from the gases at 0°, determined calorimetrically, is 41·3 kcal. The ammoniate can be purified by sublimation [79], and it does not dissolve in benzene, carbon disulphide, carbon tetrachloride, ethyl ether and other nonpolar or weakly polar solvents [64, 65], but it is sparingly soluble in alcohols. This shows that $BF_3 . NH_3$ itself has a considerable dipole moment. Its solubility in water at 25° is 36 g in 100 g H_2O. At a temperature above 125° the ammoniate decomposes according to the reaction [64]

$$4BF_3 . NH_3 \rightarrow 3NH_4BF_4 + BN$$

Cryoscopic investigations of BF_3NH_3 show that in aqueous solutions it behaves as a monomeric molecule which does not undergo association, dissociation or appreciable hydrolysis, and therefore $BF_3 . NH_3$ may be recrystallized from water [64].

$BF_3 . NH_3$ is a classical example of coordination compounds which are formed by a donor—acceptor link. This compound was first prepared by Gay-Lussac [66], and was studied in detail by Davy [67]. Davy, however, considered that boron fluoride could combine not only with one molecule of ammonia, forming $BF_3 . NH_3$ but also with two and three, giving compounds $BF_3 . 2NH_3$ and $BF_3 . 3NH_3$, which are watery liquids. On heating in air or in the presence of CO_2 or HCl, they easily lose excess of NH_3 and are again converted into the basic compound $BF_3 . NH_3$.

Other investigators [68, 69] have also studied the properties of boron fluoride monoammoniate. Laubengayer and collaborators [64] studied the reaction of boron fluoride with ammonia in particular detail. He took a definite quantity of NH_3 and BF_3 and left them at 25° until equilibrium was reached. Laubengayer's results are given in Table 14, from which it is clearly seen that only the monoammoniate of boron fluoride $BF_3 . NH_3$ is formed, which is obtained as a white, solid substance. None of the liquid products described by Davy was isolated in addition to this.

Table 14. *Intersaturability of boron fluoride and ammonia* [64]

Mols. NH_3 per mol. BF_3	Residual pressure (mm)	Mols. NH_3 per mol. BF_3	Residual pressure (mm)
0·399	71·6	1·990	112·2
1·000	1·4	2·530	174·6
1·440	49·6	2·950	225·6

Consequently the boron atom can accept only one unshared pair of electrons of the nitrogen atom of one molecule of ammonia and form a coordination compound in the ratio of 1 : 1. The compound $BF_3 . NH_3$ is probably capable, in certain conditions, of reacting further with ammonia according to the reaction

$$BF_3 . NH_3 + NH_3 \rightarrow [(NH_3)_2BF_2]^+F^-$$

But Laubengayer expresses a doubt that such an ionic diammoniate may be the liquid product observed by Davy.

I. G. Ryss and N. P. Pisarzhevskaya [63] studied the hydrolysis of BF_3NH_3 and found that the first stage of the reaction was

$$BF_3 . NH_3 + H_2O \rightarrow \overset{+}{N}H_4 + [HOBF_3]^-$$

The hydroxyfluoroboric acid ion formed is quantitatively titrated with alkali in the presence of calcium chloride and methyl orange:

$$2BF_3OH^- + 3Ca^{++} + 4OH^- \rightarrow 3CaF_2 + 2H_3BO_3$$

Laubengayer and collaborators [64] explain the considerable stability of the compound $BF_3 . NH_3$ in relation to hydrolysis by the fact that the nitrogen and boron atoms which take part in its formation are converted from atoms with coordination number 3 to atoms with coordination number 4. The increase of coordination number strongly binds the central atoms together, as a result of which, instead of a planar an ethane-like structure with tetrahedral direction of the bonds is formed. There are indications that BF_3 with NH_3 and H_2O forms, besides other products, a compound of the following composition: $(NH_4)_2O(BF_4)_2$ [70].

Coordination Compounds of BF_3 *with Argon*

Argon belongs to the inert gases and is in Group O of the periodic system of elements, but in spite of this it is activated in the presence of an aprotonic acid, boron fluoride, and like bases it forms coordination compounds with it according to the scheme

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}: + BF_3 \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}: BF_3$$

A detailed study of the system A—BF_3 by the method of thermal analysis [71] showed that argon can add to one or more molecules of boron fluoride. In particular, on a basis of freezing curves (Fig. 8) the existence of the following compounds was confirmed: A. BF_3, A. $2BF_3$, A. $6BF_3$, A. $8BF_3$ and A. $16BF_3$. These compounds are unstable and at their melting point dissociate practically completely into their components [72]. The compound A. $2BF_3$ seems to be the most stable.

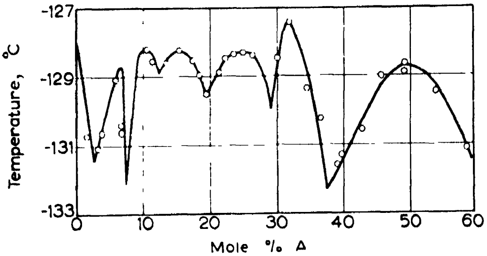
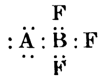


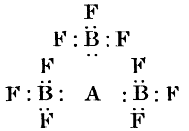
Fig. 8. The system BF_3— A. Temp. °C; mole % A.

A. I. Schatenstein [73] doubts whether chemical bonds take part in the formation of coordination compounds of boron fluoride with argon, and thinks that the formation of such compounds by the cooperation van der Waals' forces is more probable.

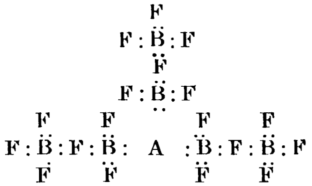
It appears to us that there are no grounds for attributing the formation of these compounds to any mechanism other than that which was decribed above for the formation of all coordination compounds of boron fluoride in general. In the given instance the boron atom with the electron sextet envelope combines with argon which has a complete octet, and forms a coordination compound. In compounds of the type A. $6BF_3$ and with a large number of molecules of BF_3, a portion of the molecules is united directly with the argon and a portion through the fluorine atoms, as shown below:



$$\begin{array}{c} \text{F} \\ :\ddot{\text{A}}:\ddot{\text{B}}:\text{F} \\ \ddot{\text{F}} \end{array}$$



$$\begin{array}{ccc} & \text{F} & \\ & \text{F}:\ddot{\text{B}}:\text{F} & \\ \text{F} & & \text{F} \\ \text{F}:\ddot{\text{B}}: & \text{A} & :\ddot{\text{B}}:\text{F} \\ \ddot{\text{F}} & & \ddot{\text{F}} \end{array}$$



$$\begin{array}{ccc} & \text{F} & \\ & \text{F}:\ddot{\text{B}}:\text{F} & \\ & \ddot{\text{F}} & \\ & \text{F}:\ddot{\text{B}}:\text{F} & \\ \text{F}\quad\ \text{F} & & \text{F}\quad\ \text{F} \\ \text{F}:\ddot{\text{B}}:\text{F}:\ddot{\text{B}}: & \text{A} & :\ddot{\text{B}}:\text{F}:\ddot{\text{B}}:\text{F} \\ \text{F}\quad\ \ddot{\text{F}} & & \text{F}\quad\ \ddot{\text{F}} \end{array}$$

In this way the electrons of the completed octet envelope may also be activated in certain conditions.

To conclude this section we introduce a composite table (Table 15) of the physico-chemical characteristics of some coordination compounds of boron fluoride with inorganic substances.

Table 15. *Compounds of* BF_3 *with inorganic substances* [74]

Compound	m. p. (°C)	b. p. (°C/mm)	sp. gr.	Literature references
$NaBF_4$	Decomposes above 400°	—		[7, 10]
KBF_4	Decomposes above 400°	—	—	[7, 10]
$Ca(BF_4)_2$	Decomposes at 300–500°	—		[7]
$[Cu(H_2O)_6][BF_4]_2$	—	—	—	[10]
$[Ag(H_2O)][BF_4]$	—	—	—	[10]
$[Zn(H_2O)_6][BF_4]_2$	Hygroscopic	—	—	[7]
$[Sr(H_2O)_4][BF_4]_2$	—	—	—	[10]
$[Cd(H_2O)_6][BF_4]_2$	—	—	—	[7, 10]
$[Ba(H_2O)_2][BF_4]_2$	—	—	—	[7]
$HgO . BF_4 . HF . H_2O$	Hygroscopic	—	—	[7, 10]
$[Mg(H_2O)_6][BF_4]_2$	—	—	—	[7]
$[Ag(NH_3)_2][BF_4]$	—	—	—	[9]
$[Ag(NH_3)_4][BF_4]$	—	—	—	[10]
$[Zn(NH_3)_4][BF_4]_2$	—	—	—	[10]
$[Zn(NH_3)_6][BF_4]_2$	—	—	—	[9]
$[Cd(NH_3)_6][BF_4]_2$	—	—	—	[9]
$[Cr(NH_3)_6][BF_4]_3$	—	—	—	[9]
$[Co(NH_3)_6][BF_4]_3$	—	—	—	[9]
$[Ni(NH_3)_6][BF_4]_2$	—	—	—	[9, 10]
$NaBF_3OH$	—	Decomposes at 400°	—	[14]
KBF_3OH	—	Decomposes at 400°	—	[14]
$Na_2SO_4 . BF_3$	310	—	—	[14]
$K_2SO_4 . BF_3$	240	Decomposes at 260°	—	[14]
$Cs_2SO_4 . BF_3$	250	—	—	[14]
$Na_3PO_4 . 3BF_3$	320—350°	Decomposes above 400°	—	[14]
$K_3PO_4 . 3BF_3$	320—350°	Decomposes above 400°	—	[14]
$Na_4P_2O_7 . 4BF_3$	360	Decomposes	—	[14]
$K_4P_2O_7 . 4BF_3$	360	Decomposes	—	[14]
$NH_3 . BF_3$	163	Sublimes	1·864/25°	[64]
$BF_3 . H_2O$	5·4—6·0	Decomposes	1·777/15°	[21, 22]
	4·5	62/2		[21]
$BF_3 . 2H_2O$	4·6— 5	58—60/1·2	1·632/20°	[21, 22]
	5·9—6·1		1·6315/20°	[23]
$BF_3 . 5H_2O$	—	—	1·580	[20]
$BF_3 . H_3PO_4$	—105*	Decomposes	1·903/20°	[45]
$H_4P_2O_7 . 2BF_3$	— 82*	Decomposes	1·930/20°	[45]
$BF_3 . HPO_3$	— 53*	Decomposes	1·992/20°	[45]
$HF . BF_3 . H_2O$	—	—	1·750	[14, 51]
$Na_2O . 4BF_3$	—	Decomposes with H_2SO_4	—	[16]

* Solidification point.

Table 15 *(continued)*

Compound	m. p. (°C)	b. p. (°C/mm)	sp. gr.	Literature references
$BF_3 . H_2S$	—137	—	—	[31, 32]
$BF_3 . 2 \cdot 5H_2SO_4$	—	Viscous liquid	—	[18]
$BF_3 . SO_2F_2$	—140·8	—	—	[57]
$BF_3 . SO_2$	—96·0	—	—	[53]

2. COORDINATION COMPOUNDS OF BORON FLUORIDE WITH ORGANIC SUBSTANCES

The coordination compounds of BF_3 with organic substances are of particular interest. These compounds are considerably more numerous than the compounds with inorganic substances. Many of them are used as active catalysts for alkylation, condensation, polymerization and other reactions. Coordination compounds of BF_3 with organic substances are formed as intermediate products in all reactions in which BF_3 is used as a catalyst. Some of them, for example the coordination compounds of boron fluoride with salts of carboxylic acids, are used for protecting wool against moths.

With organic compounds containing hydroxyl, as with water, boron fluoride forms coordination compounds in which there are one or two molecules of organic substance per molecule of BF_3. Compounds of such a type acquire the character of strong acids and are the most active catalysts. They are usually fuming liquids or solid substances which are difficult to crystallize; they are readily decomposed by water. Coordination compounds of BF_3 with substances containing nitrogen, and also with ethers, usually contain one molecule of ether or nitrogen-containing substance per molecule of BF_3.

Coordination Compounds of BF_3 *with Alcohols*

The first attempts to isolate the products of the reaction of BF_3 with alcohols were made by Gasselin [75]. He found that on distilling a saturated solution of boron fluoride in methyl alcohol, the mono- and dimethoxyfluoranhydrides of boric acid CH_3OBF_2 and $(CH_3O)_2BF$, the methyl etherate of boron fluoride, HF, HBF_4 and H_3BO_3 are obtained. According to Gasselin [76], the reaction of boron fluoride with ethyl alcohol proceeds as follows:

$$7BF_3+7C_2H_5OH \rightarrow C_2H_5OBF_2+3BF_3.O(C_2H_5)_2+2HBF_4+2HF+H_3BO_3$$

However, as later investigations showed [16], alcohols and also phenols form coordination compounds with boron fluoride mainly of two types:

$BF_3 . ROH$ and $BF_3 . 2ROH$. In their properties they all recall the compounds of boron fluoride with water and mineral acids. They have the character of strong acids, but are weaker than boron fluoride hydrates, as is seen from a comparison of their electrical conductivity [33], given in Table 16.

By a study of the electrical conductivity of the system CH_3OH-BF_3 at 25° (Fig. 9) the existence of a compound $BF_3 . CH_3OH$ was found [77] and it was shown to have the properties of an acid and could be regarded as methoxyfluoroboric acid of the structure $[CH_3OBF_3]^-H^+$. By treating this acid with red mercuric oxide, mercury methoxyfluoroborate is obtained [78]:

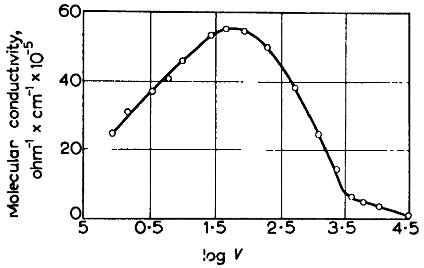


Fig. 9. The system $CH_3OH—BF_3$. Molecular conductivity $ohm^{-1} . cm^{-1} . 10^{-5}$ log V.

$$2(CH_3OBF_3)H + HgO \rightarrow (CH_3OBF_3)_2Hg + H_2O$$

Table 16. *Electrical conductivity of certain coordination compounds of boron fluoride* [33]

Compound	Electrical conductivity at 25°, ($ohm^{-1} . cm^{-1}$)		
	Specific	Equivalent	Molecular
$BF_3 . H_3PO_4$	0·00722	0·0205	0·615
$H_4P_2O_7 . 2BF_3$	0·00670	0·2700	1·080
$BF_3 . H_2O$	0·03860	0·3400	1·880
$BF_3 . 2H_2O$	0·16600	—	—
$BF_3 . CH_3OH$	0·01371	0·9660	—
$BF_3 . C_2H_5OH$	0·00854	0·7180	—
$BF_3 . O(C_2H_5)_2$	0·00280	0·3500	—
$BF_3 + H_2SO_4$*	0·03560	—	—
H_2SO_4 (100·1%)	0·04350	0·1580	2·316
H_3PO_4	0·05100	0·8850	2·660
HNO_3	0·02680	—	—
H_2O (distilled)	0·00045	—	0·0157

* Saturated solution of boron fluoride in 98 % sulphuric acid.

On treatment with sodium methylate or ammonia, methoxyfluoroboric acid decomposes with the formation of sodium fluoroborate or boron fluoride ammoniate:

$$2(CH_3OBF_3)^-H^+ + CH_3ONa \rightarrow NaBF_4 + CH_3OBF_2 + 2CH_3OH$$
$$(CH_3OBF_3)^-H^+ + NH_3 \rightarrow BF_3 . NH_3 + CH_3OH$$

By a study of the electrical conductivity of the system $C_2H_5OH-BF_3$, the formation of a coordination compound $BF_3 . C_2H_5OH$, which readily dissociates into H^+ and $[C_2H_5OBF_3]^-$, was confirmed.

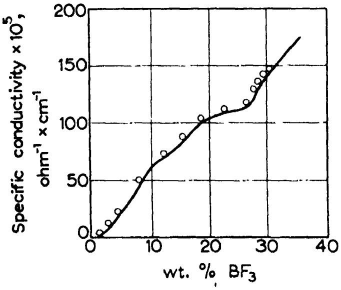


Fig. 10. The system $C_6H_5OH—BF_3$ at 50°C. Specific conductivity × 10^5 $ohm^{-1} . cm^{-1}$. Wt. % BF_3.

In addition to this the formation of a compound $BF_3 . 2C_2H_5OH$ was demonstrated, which is as strong an acid as sulphuric.

Also on the basis of a graph of the electrical conductivity of the system $BF_3—C_6H_5OH$ at 50°C (boron fluoride in molten phenol; Fig. 10) the formation of a coordination compound $BF_3 . 2C_6H_5OH$ was confirmed in addition to the compound $BF_3 . C_6H_5OH$ [79].

The compound $BF_3 . C_6H_5OH$ has the properties of a strong acid and adds fairly readily to propylene with the formation of *iso*propyl phenyl ether. All these investigations leave no doubt that the substances isolated by Gasselin were products of the decomposition of boron fluoride coordination compounds with alcohol, which readily takes place on distillation under atmospheric pressure.

The thermal stability of coordination compounds in the primary alcohols series diminishes as their molecular weight increases.

Among the isomeric alcohols the coordination compounds which are thermally most stable are given by primary and the least stable by tertiary alcohols, i. e. the more easily the alcohol is dehydrated, the less stable are its coordination compounds with BF_3.

The most stable coordination compounds are those in which there are two molecules of alcohol to one molecule of BF_3. These compounds possess even higher electrical conductivity. Thus, compounds of the type $BF_3 . ROH$, like boron fluoride monohydrate, are unstable and cannot be distilled without decomposition. Compounds of the type $BF_3 . 2ROH$ are quite stable, and some of them can be distilled *in vacuo.* All primary normal alcohols from methyl to butyl inclusive, and also ethylene glycol chlorhydrin, phenol and benzyl alcohol form them. In nitrobenzene solution they conduct an electric current, but the compounds $BF_3 . C_2H_5OH$ and $BF_3 . C_4H_9OH$ do not dissociate, while the compound $BF_3 . 2ClCH_2CH_2OH$ and especially $BF_3 . 2C_6H_5CH_2OH$ readily decompose into their components. The compound $BF_3 . 2C_6H_5CH_2OH$ on heating *in vacuo* at 40—50° evolves BF_3 quantitatively, but on heating at ordinary pressure it decomposes, splitting off $BF_3 . 2H_2O$ and forming high molecular compounds of the general formula $(C_6H_5CH)_x$, among which Cannizzaro detected stilbene [80].

In a similar way other alcohols combined with BF_3 are converted into complex hydrocarbons. The coordination compounds of BF_3 with secondary alcohols are very unstable, and on distillation they easily split off boron fluoride dihydrate and form olefines which are readily converted into highly polymerized compounds.

Glycols with BF_3 form coordination compounds of the type $[RCH(OH)CH_2OH] . BF_3$.

Alcoholates are capable of giving coordination compounds with boron fluoride [3] of the general formula $[BF_3OR]^-Na^+$.

Compounds of boron fluoride with one molecule of alcohol may by their structure be regarded as strong protonic alkoxyfluoroboric acids $[BF_3OR]^-H^+$. In relation to them alcohols behave like bases and form

Table 17. *Coordination compounds of* BF_3 *with alcohols*

Compound	m. p. (°C)	b. p. (°C/mm)	d_4^{20}	Literature references
$BF_3 . CH_3OH$	—19·4	Decomposes	1·4160	[77, 78]
$BF_3 . 2CH_3OH$		58 - 59/4	1·3115	[21, 22]
$BF_3 . C_2H_5OH$	—19·0	Decomposes	1·3530	[16, 79]
$BF_3 . 2C_2H_5OH$	—	51—52/1·5	1·1638	[21, 22]
$BF_3 . 2\text{-}n\text{-}C_3H_7OH$	—	56/2	1·1059	[21, 22]
$BF_3 . 2\text{-}n\text{-}C_4H_9OH$	—	64—65/3	1·0442	[21, 22]
$BF_3 . CH_2OH—CH_2OH$	40—42	Decomposes	—	[79]
$BF_3 . 2CH_2OH—CH_2Cl$	—	59/2	1·4009	[21, 22]
$BF_3 . 2C_6H_5CH_2OH$	40·0	—	—	[82]
$BF_3 . C_6H_5OH$	—	Decomposes	1·2440	[79]
$BF_3 . 2C_6H_5OH$	—	—	—	[79]

salts, as in reactions of strong acids, for example perchloric, with weak acids [81]:

$$[BF_3OR]^-H^+ + ROH \rightarrow [BF_3OR]^-[RH_2O]^+$$
$$HClO_4 + HONO_2 \rightarrow [ClO_4]^-[(HO)_2NO]^+$$
$$HClO_4 + H_3PO_4 \rightarrow [ClO_4]^-[(HO)_4P]^+$$
$$HClO_4 + RCOOH \rightarrow [ClO_4]^-[RC(HO)_2]^+$$
$$HClO_4 + H_2O \rightarrow [ClO_4[^-(H_3O)^+$$

The properties of some coordination compounds of BF_3 with alcohols are given in Table 17.

Coordination Compounds of BF_3 *with Carboxylic Acids*

According to Landolph's data [83], boron fluoride has a dehydrating action on acids such as acetic, and enables acetic anhydride to be obtained.

In earlier investigations [84], Meerwein considered it probable that acetic acid and BF_3 would form a compound $H[CH_3COO \cdot BF_3]$.

These data do not inspire complete confidence and are probably the result of adopting as initial compounds the decomposition products formed on distillation, because the latest investigations of many authors including Meerwein himself [21, 22] have conclusively shown that boron fluoride forms with carboxylic acids, as with alcohols, coordination compounds of the following two types:

$$\text{(I)}\quad BF_3 \cdot 2RCOOH \quad \text{and} \quad \text{(II)}\quad BF_3 \cdot RCOOH$$

By analogy with the alcohols the structure of such compounds may be represented by the following structural formulae:

$$BF_3 \cdot 2RCOOH \quad \text{or} \quad [RCOO \cdot BF_3]^-[H_2OCOR]^+$$
$$BF_3 \cdot RCOOH \quad \text{or} \quad [RCOO \cdot BF_3]^-H^+$$

The acid properties of the compounds of both types are considerably stronger than those of the corresponding carboxylic acids, so that they can be fully related to strong acids.

All monobasic aliphatic acids absorb one molecule of BF_3 per one or two molecules. Aromatic acids (benzoic and phenylacetic) in chloroform solution absorb one molecule of boron fluoride per molecule, but in addition, compounds are obtained which split off BF_3 completely on heating *in vacuo*.

Dibasic acids (oxalic, succinic and malonic) with BF_3 in ether solution also combine in the ratio 1 : 1.

The stability of coordination compounds of boron fluoride with carboxylic acids depends on the structure of the acids, their molecular weight, the presence of substituents and their nature.

Coordination compounds of the first type in usual conditions are liquid substances, but those of the second type are solid products. As for water and alcohols, the most stable are the coordination compounds $BF_3 . 2RCOOH$. Some of these can be distilled without appreciable decomposition even in a partial vacuum. On introducing boron fluoride into these compounds they are comparatively easily converted into solid coordination compounds of composition $BF_3 . RCOOH$. On heating, the latter split off one molecule of BF_3 from two molecules and are again converted into liquid compounds of composition $BF_3 . 2RCOOH$. The liquid compound $BF_3 . HCOOH$ and the solid $BF_3 . CH_3CH = CHCOOH$ are very unstable and decompose on keeping.

In the series of unsubstituted aliphatic acids the stability of the coordination compounds decreases from acetic to butyric acid. Thus, $BF_3 . 2CH_3COOH$ distils at atmospheric pressure without decomposition, but $BF_3 . 2CH_3CH_2COOH$ at the same time undergoes cleavage.

Table 18. *Coordination compounds of* BF_3 *with carboxylic acids*

Compound	m.,p. (°C)	b. p. (°C/mm)	d_4^{20}	Literature references
$BF_3 . HCOOH$	—20	Decomposes on keeping	—	[22]
$BF_3 . 2HCOOH$	—	43—44/11	1·5145	[22]
$BF_3 . CH_3COOH$	23—24	Decomposes	—	[22]
$BF_3 . 2CH_3COOH$	—	53—54/10	1·3420	[82]
		140/746	1·3510/21°	[22]
$BF_3 . CH_3CH_2COOH$	28—29	—	—	[82]
$BF_3 . 2CH_3CH_2COOH$	—	60—60·5/12	1·2283	[22]
		62—63/17	1·2380/23°	[16]
$BF_3 . CH_3CH_2CH_2COOH$	23—30	—	—	[22, 85]
$BF_3 . 2CH_3CH_2CH_2COOH$	—	64/11	1·1506	[22]
$BF_3 . 2(CH_3)_2CHCOOH$	—	68—70/15	—	[86]
$BF_3 . CH_3CH = CHCOOH$	35—36	—	—	[82]
$BF_3 . 2CH_3CH=CHCOOH$	—	81—82/12·5	—	[22]
$BF_3 . CH_3CH(OH)COOH$	—	Decomposes	—	[85]
$BF_3 . 2CH_2ClCOOH$	—	95—100/18	—	[82]
$BF_3 . Cl_2CHCOOH$	Stable at —15° and below	—	—	[22]
$BF_3 . C_6H_5COOH$	70	Decomposes	—	[22]
	90—91·5			[16]
$BF_3 . 2C_6H_5COOH$	98	Decomposes	—	[3, 16]
$BF_3 . (COOH)_2$	57—58 (decomposes)	—	—	[22]
$BF_3 . HOOCCH_2COOH$	75—78	—	—	[22]
$BF_3 . HOOC(CH_2)_2COOH$	82—84 (decomposes)	—	—	[22]

The presence of polar or easily polarizable groups situated in the vicinity of the carboxyl group exerts a great influence on the stability of coordination compounds of boron fluoride with carboxylic acids. This influence is visibly demonstrable in compounds of acetic and chloracetic acids. The coordination compound of boron fluoride with acetic acid is so stable that it does not decompose even in the vapour state and is easily distilled. The compound with chloracetic acid already decomposes at 80° and gives off all its BF_3. The compound with dichloracetic acid probably exists only at $-15°$ and below, and trichloracetic acid according to certain data [16] does not form coordination compounds with BF_3. The physico-chemical characteristics of certain coordination compounds of BF_3 with acids are given in Table 18.

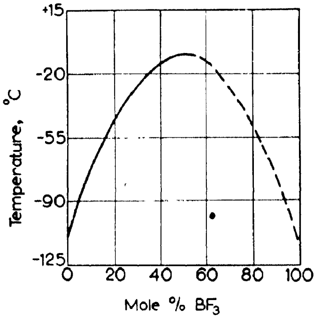


Fig. 11. The system BF_3—$(CH_3)_2O$. Temp. °C; mole % BF_3.

Coordination Compounds of BF_3 *with Ethers and Esters*

Coordination compounds of boron fluoride with ethers and esters which are weakly associated substances, contain one mol. of ether per mol. of BF_3. They are usually obtained by saturating absolute ethers with boron fluoride at room temperature or by distilling coordination compounds of boron fluoride with alcohols. When, for example, a saturated solution of boron fluoride in methyl alcohol is distilled, boron fluoride methyl etherate is formed in 50 per cent yield [75]. Boron fluoride ethyl etherate is formed in a similar way [76].

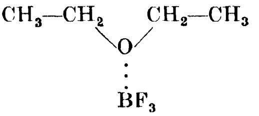
In Fig. 11 a graph of the system BF_3—$(CH_3)_2O$ is given.

The coordination compounds of boron fluoride with simple alkyl ethers are liquids, often very stable, which can be distilled without decomposition, although there are indications that the methyl- and ethyl etherates (I) of boron fluoride dissociate below the boiling point according to the reaction [87]

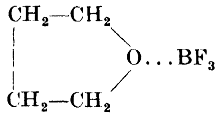
$$BF_3 \cdot OR_2 \rightleftarrows BF_3 + OR_2$$

Dissociation probably also takes place in the case of other compounds. There is therefore always a certain quantity of free boron fluoride in the etherates.

The coordination compounds of arylalkyl ethers (anisole and phenetole) are viscous, transparent liquids which are very unstable and readily split off BF_3 on distillation. Anisole, for example, as has already been shown, absorbs boron fluoride very well but liberates it quantitatively on heating to 100—150°, and the coordination compound of anisole with BF_3 is often used for the preparation of boron fluoride. Dibenzyl ether does not form coordination compounds with BF_3 on account of steric hindrance [16]. At the same time, tetrahydrofuran, in which there is no steric hindrance, with boron fluoride gives a coordination compound (II) which is more stable than the methyl-, ethyl- and *iso*propyl etherates of boron fluoride [88].



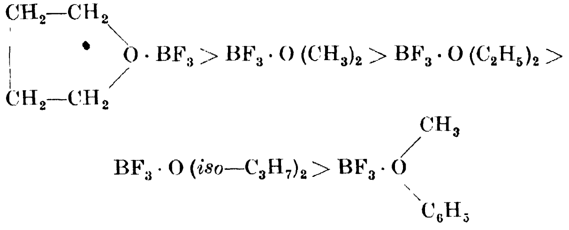
(I) ,



(II)

The presence of electronegative groups alongside the ether oxygen, as in the case of the chloracetic acids, decreases the stability of the coordination compounds of boron fluoride with ethers. For example, boron fluoride *a*, *a*-dichlorodiethyl etherate, in contrast to boron fluoride ethyl etherate, readily splits up into its components on heating to 100—110°.

The stability of the following BF_3 etherates decreases from left to right [88]:



In Table 19 the physical properties of certain etherates are given.

Coordination compounds of boron fluoride with esters of fatty acids are also of 1 : 1 composition. Their stability depends on the structure of the esters. Compounds of boron fluoride with esters of monobasic fatty acids are fairly stable crystalline substances, but

Table 19. *Physical properties of boron fluoride etherates* [87]

Properties	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>O\,.\,BF_3$	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>O\,.\,BF_3$	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>O\,.\,BF_3$
m. p. (°C)	—14	—98	—60·4
b. p. (°C)	126·6	127·0	125·7
sp. gr. (d^{25})	1·239	1·176	1·125
Refractive index, n_D^{20}	1·302	1·327	1·348
Molecular volume	102·1	120·9	139·9
Parachor	220·6	256·2	294·6
Molecular refraction	17·6	22·04	26·63
Equation for calculating the vapour pressure in mm mercury (T in °K)	$\log p = \frac{-2650}{T} + 9{\cdot}58$	$\log p = \frac{-2860}{T} + 10{\cdot}05$	$\log p = \frac{-2845}{T} + 10{\cdot}02$
Heat of vaporization, kcal/mole	8·8	—	8·8
Heat of formation, kcal/mole	13·9 ± 0·7	—	12·5 ± 1·0
Dipole moment in C_6H_6 at 25°, D	4·35 ± 0·12	5·07 ± 0·08	4·92 ± 0·38
Trouton constant	30·5	33·0	32·8

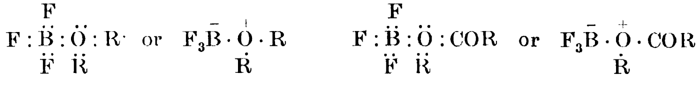
compounds with esters of monobasic aromatic acids, for example with phenyl acetate and ethyl benzoate, are rather unstable liquids which readily liberate all the BF_3 on distillation *in vacuo*. The coordination compounds with both ethyl chloracetate and ethyl trichloracetate are not very stable. The compounds of BF_3 with esters of dibasic aliphatic acids are unstable crystalline products. Thus, diethyl oxalate and diethyl malonate form crystalline compounds of 1 : 1 composition, which on distillation *in vacuo* split off BF_3 with partial decomposition.

The monomethyl ether of glycol monoacetate absorbs 2 moles BF_3 per mole and forms a viscous liquid which does not crystallize. When an attempt is made to distil it BF_3 is split off and resinous products remain [16]. Glycol diacetate yields long, needle-shaped crystals on standing with BF_3 for some time [16].

In Table 20 the properties of coordination compounds of BF_3 with different ethers and esters are given.

In coordination compounds of boron fluoride with ethers, the organic molecules are activated. The alkyl groups linked by the ether linkage can easily be split off. Compounds of boron fluoride with ethers are therefore often used as alkylating agents.

The mechanism of the formation of coordination compounds of boron fluoride with ethers and esters does not differ in principle from the mechanism for the compounds described above. As numerous investigations of the properties and character of the bond of boron fluoride dimethyl etherate and other compounds [87, 88, 94, 95] showed, there is between the boron fluoride and the ethers and esters a donor—acceptor bond of the usual character for BF_3 where the donor is the ether oxygen which gives up an unshared pair of electrons, and the acceptor is the sextet boron which vigorously attracts a pair of electrons in order to make up its electron envelope to an octet [96]. In this way, the structure of these coordination compounds may be represented by the following formulae:



$$\begin{matrix} & F & & & \\ F: & \ddot{B} & : & \ddot{O} & :R \\ & \ddot{F} & & R & \end{matrix} \quad \text{or} \quad F_3\overset{-}{B}\cdot\underset{R}{\overset{+}{\dot{O}}}\cdot R \qquad \begin{matrix} & F & & & \\ F: & \ddot{B} & : & \ddot{O} & :COR \\ & \ddot{F} & & R & \end{matrix} \quad \text{or} \quad F_3\overset{-}{B}\cdot\underset{R}{\overset{+}{\dot{O}}}\cdot COR$$

These formulae are at present universally acknowledged and have entered into our chemical usage. For boron fluoride ethyl etherate this structure is confirmed by the good agreement between the found (294·6) and calculated (295·4) values of the parachor [97].

Compounds of boron fluoride with ethers and esters possess high polarity and have a large dipole moment, as is seen from Table 19. However, their electrical conductivity is considerably lower than the conductivity of the well ionized coordination compounds of boron fluoride with compounds containing hydroxyl [33].

As Laubengayer and collaborators [94, 98] found, when coordination compounds with ethers are formed by means of boron fluoride, although the reacting molecules do not change their composition they are very much deformed: the boron fluoride molecule changes its planar structure into a tetrahedral one with the boron atom at the centre of the tetrahedron, linked with the three fluorine atoms and with one atom of oxygen, and this in its turn leads to an increase in the interatomic distance B—F. As electron diffraction investigations show, in the formation of boron fluoride methyl etherate the molecule of dimethyl ether remains unchanged, the distance B—F increases from 1·30 Å in BF_3 to 1·43 Å in $BF_3 . O(CH_3)_2$, and the distance B—O is 1·50 Å, i. e. it corresponds to a chemical link acting at a distance of about 2·5—3 Å. It is thus clear that the coordination compound $BF_3 . O(CH_3)_2$ has a chemical bond formed as a result of the new valency of the boron atom and may be represented by the following structure:

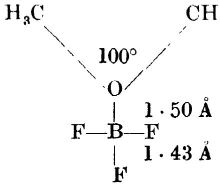


Table 20. *Compounds of* BF_3 *with ethers and esters*

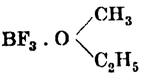
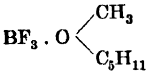
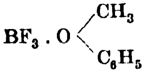
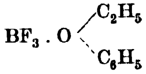
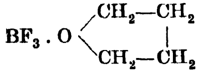
Compound	m. p. (°C)	b. p. (°C/mm)	d_4^{20}	Parachor		Literature reference
				Found	Calc.	
$BF_3 . O(CH_3)_2$	—14	126·6	1·239/25°			[87]
		128·0	1·241	220·6	222·0	[89]
 $BF_3 . O\begin{matrix}CH_3\\C_2H_5\end{matrix}$	—98	127·0	1·176/25°	—	—	[87]
$BF_3 . O(C_2H_5)_2$	—60·4	125·7	1·125/25°	294·6	300·0	[87]
$BF_3 . O(iso\text{-}C_3H_7)_2$	—68	126—127/777	1·135/13°			[89]
		—	—	—	—	[88]
 $BF_3 . O\begin{matrix}CH_3\\C_5H_{11}\end{matrix}$	—41	54·8—55/10	—	—	—	[90]
$BF_3 . O(iso\text{-}C_3H_{11})_2$	—	78—79/22	—	—	—	[91]
$BF_3 . O(CHClCH_3)_2$	—	Unstable	—	—	—	[62]
 $BF_3 . O\begin{matrix}CH_3\\C_6H_5\end{matrix}$	—12—13	Decomposes	—	—	—	[90]
 $BF_3 . O\begin{matrix}C_2H_5\\C_6H_5\end{matrix}$	—	Unstable	—	—	—	[3]
	—	—	—	—	—	[88]
Dioxane . $BF_3 . H_2O$	128—130	—	—	—	—	[22]
Dioxane . $BF_3 . 2H_2O$	142	—	—	—	—	[22]
Cineole . $BF_3 . H_2O$	71·3	—	—	—	—	[22]
Cineole . $BF_3 . 2H_2O$	59·5—61	—	—	—	—	[22]
$BF_3 . HCOOCH_3$	23·5	94/772	—	—	—	[92]
	23·5	92·5	1·409/31·5°	228·4	227·8	[89]
$BF_3 . HCOOC_2H_5$	—	102/748	1·311/25°			[16]
	3·0	103	1·323/19°	262·7	266·8	[89]
$BF_3 . CH_3COOCH_3$	61·5	112/772	1·249/61·5°	269·8	266·8	[89]
	60·0	110/739	—			[16]
$BF_3 . CH_3COOC_2H_5$	31·0	123/772	1·223/42°	303·1	305·8	[89]
	26·0	119/739				[16]
$BF_3 . CH_3COOC_3H_7$	—	126/743	1·170/23°	—	—	[16]
$BF_3 . CH_2ClCOOC_2H_5$	—	Decomposes *in vacuo*	—	—	—	[16]
$BF_3 . CCl_3COOC_2H_5$	—	Decomposes *in vacuo*	—	—	—	[16]
$BF_3 . CH_3CH_2COOC_2H_5$	33·0	116/747	—	—	—	[16]
$BF_3 . (COOC_2H_5)_2$	Decomp.	—	—	—	—	[16]
$BF_3 . C_2H_5OOCCH_2COOC_2H_5$	Decomp.	—	—	—	—	[16]
$BF_3 . CH_3COOC_6H_5$	40—55	—	—	—	—	[16]
$BF_3 . C_6H_5COOC_2H_5$	Decomp.	—	—	—	—	[16]

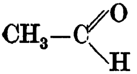
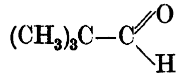
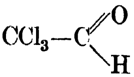
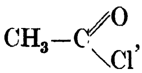
Table 20 *(continued)*

Compound	m. p. (°C)	b. p. (°C/mm)	d_4^{20}	Parachor		Literature reference
				Found	Calc.	
$BF_3 . CH_3OOCCH_2CH_2COOCH_3$	Needle-shaped crystals	—	—	—	—	[16]
$CH_3OCH_2CH_2COOCH_3 . 2BF_3$	Decomp.	—	—	—	—	[16]
$BF_3 . p\text{-}CH_3C_6H_4COOCH_3$	146—150	—	—	—	—	[16]
$BF_3 . HOCH_2COOCH_3$	—	60/3	—	—	—	[93]
$BF_3 . HOCH_2COOC_2H_5$	31	119/739	1·276	—	—	[16]
$(p\text{-}CH_3C_6H_4O)_3PO . BF_3$	—	Decomposes	1·246	—	—	[43]

If molecules of BF_3 and $(CH_3)_2O$ were linked on account of weak van der Waals' forces acting at a distance of 3—4 Å, the distance B—O would be greater and the molecules would not undergo any substantial deformation. The participation of chemical forces (together with van der Waals' forces) in the formation of the coordination compounds in question is also confirmed by the energy of their formation, given in Table 19. Thus, the heat of formation of $BF_3 . O(CH_3)_2$ from ether and boron fluoride is 13·9 kcal/mole, and for $BF_3 . O(C_2H_5)_2$ it is 12·5 kcal/mole, i. e. considerably more than the energy of the van der Waals' reaction, which is 0·5—5 kcal/mole, but somewhat less than the energy of the ordinary chemical reaction, which is 50—100 kcal/mole. Consequently it is impossible to identify the B—O bond in etherates with the ordinary chemical bond.

Coordination Compounds of BF_3 *with Aldehydes and Ketones*

Among the scores of coordination compounds of boron fluoride with organic substances the addition products of BF_3 to carbonyl derivatives are few. Meanwhile the study of such compounds is of great interest, because the carbonyl group, as is known, enters into the composition of such compounds as esters, ketones, aldehydes and acid anhydrides, and an explanation of the character of the linkage of boron fluoride with them would enable this type of compound to be better known.

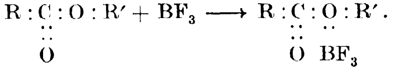
Brown and collaborators [99] studied in detail the reaction of diborane B_2H_6 with carbonyl compounds of different structure and compared them with the compounds of boron fluoride which in many respects is similar to diborane. Boron fluoride forms coordination compounds with the  $CH_3-C\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}}$,  $(CH_3)_3C-C\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}}$,  $CCl_3-C\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}}$ and  $CH_3-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\lessgtr}}$, adding to the carbonyl group in the ratio of 1 : 1. Consequently the statement of some investigators that the oxygen atom connected to the carbonyl group by a double bond is not capable of coordinating with boron fluoride because the coordination of the oxygen atom is possible only in the presence of a hybrid sp^3 orbit, which is absent from the carbonyl group, is not valid.

The stability of such compounds, however, is not uniform. Aldehydes and ketones which react easily with diborane form stable products with BF_3. Acetone, for example, forms a crystalline compound of m. p. 35—40°, which decomposes only at 50°. Trimethylacetaldehyde readily adds 1 molecule of BF_3 with the formation of a white, crystalline coordination compound stable at room temperature. BF_3 also forms a coordination compound with acetaldehyde, but the reaction is accompanied by considerable polymerization of the acetaldehyde, and therefore $CH_3CHO.BF_3$ is very difficult to isolate. Benzaldehyde and camphor form addition products with BF_3 [14].

The compounds $HC{\diagup O \atop \diagdown Cl}$, $CH_3C{\diagup O \atop \diagdown Cl}$ and $CCl_3C{\diagup O \atop \diagdown H}$, which in general do not react with diborane, form coordination compounds with BF_3, but these compounds are very unstable and exist only at temperatures from —50 to —80°. For example, acetyl chloride gives with BF_3 a complex $CH_3COCl . BF_3$, melting at —70°, but easily dissociating into its components at a higher temperature [90]. The addition product of BF_3 to phosgene exists only at a temperature of —120° [99]. By the method of physico-chemical analysis it was also found that with phosgene BF_3 forms the coordination compounds $BF_3 . COCl_2$ and $BF_3 . 2COCl_2$ [100].

Brown and collaborators [99] expected that the esters $HCOOCH_3$ and $CH_3COOC_2H_5$, which react with diborane slowly, would form addition products with boron fluoride with a stability intermediate between the compounds with aldehydes and with halogeno-aldehydes, but in fact as already stated above the coordination compounds of BF_3 with esters and in particular with $HCOOCH_3$ and $CH_3COOC_2H_5$ are very stable and can be distilled without appreciable decomposition at atmospheric pressure [16].

There is no doubt that the high stability of these compounds is due to the fact that their formation is brought about at the expense of the ether (and not the carbonyl) oxygen atom by means of a donor-acceptor bond:



$$R:\underset{\underset{O}{\vdots}}{C}:O:R' + BF_3 \longrightarrow R:\underset{\underset{O}{\vdots}}{C}:\underset{\underset{BF_3}{\vdots}}{O}:R'.$$

With aldehydes and halogeno-anhydrides the link is probably brought about at the expense of van der Waals' forces, and therefore the corresponding coordination compounds are not stable and can exist only at very low temperatures.

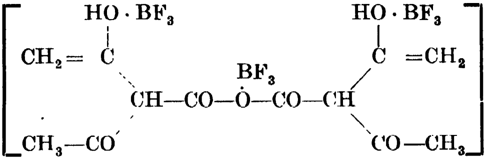
Coordination Compounds of BF_3 with Anhydrides of Carboxylic Acids and with Organic Compounds Containing Sulphur

With anhydrides BCl_3 and $SbCl_5$ give chloroanhydrides [3]. Boron fluoride in similar reactions does not form fluoranhydrides of acids but gives coordination compounds of different composition.

Acetic anhydride with BF_3 in the cold gives a crystalline derivative — a coordination compound of diacetoacetic anhydride [21]. Its formation may be represented by the scheme

$$5(CH_3CO)_2O + 7BF_3 \rightarrow 4CH_3COOH\,.\,BF_3 +$$
$$+\ (CH_3CO)_2CHCOOCOCH\ (COCH_3)_2\,.\,3BF_3$$

or



This compound does not fume in air but on heating it readily decomposes with evolution of CO_2 and formation of acetylacetone.

The indications of Nieuwland and collaborators [16] and Morgan [92] of the fact that with acetic anhydride BF_3 forms a coordination compound $BF_3\,.\,O(COCH_3)_2$ of m. p. 194° (according to other data 190°) are probably incorrect.

Propionic, butyric and *iso*butyric anhydrides form with BF_3 compounds of monoacylanhydrides of the structure $RCOCH(R)COOCOCH(R)COR\,.\,3BF_3$. When they decompose, they decompose mainly into monoketones and partly into β-diketones.

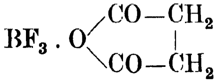
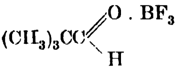
When BF_3 is passed over succinic anhydride an addition product  $BF_3\,.\,O\begin{matrix}\diagup CO-CH_2\\ \qquad |\\ \diagdown CO-CH_2\end{matrix}$ is obtained [90], which is unstable and readily decom-

Table 21. Compounds of BF_3 with ketones, aldehydes and acid anhydrides

Compound	m. p. (°C)	Literature reference
 $(CH_3)_3CC\begin{matrix}\diagup O\,.\,BF_3\\ \diagdown H\end{matrix}$	White crystals	[99]
$CH_3COCl\,.\,BF_3$	—70	[90]
$CH_3COCH_2COCH_3\,.\,BF_3$	43·0	[82]
$C_6H_5COCH_2COCH_3\,.\,BF_3$	155·0	[82]
$C_6H_5COCH_2COC_6H_5\,.\,BF_3$	191·0	[82]
$(CH_3CO)_2CHCOOCOCH(COCH_3)_3\,.\,3BF_3$	192—193	[21]
$(CH_3CO)_2O\,.\,BF_3$	190	[92]
	194	[16]

poses on heating above 70°. Some coordination compounds with ketones, aldehydes and acid anhydrides are given in Table 21.

Boron fluoride coordination compounds in which the sulphur atom of an organic substance would be the donor of a pair of electrons are not described in the literature. It is, however, known that boron chloride, which is a weaker aprotonic acid than boron fluoride, with di*iso*butyl sulphide forms di*iso*butyl sulphide boron chloride $BCl_3 . S(iso\text{-}C_4H_9)_2$ with b. p. 87° (1—2 mm), but with diethyl sulphide it gives diethyl sulphide boron chloride of b. p. 90° (1—2 mm) [101]. There is no doubt that boron fluoride is also capable of forming coordination compounds with mercaptans and alkyl sulphides.

Coordination Compounds of BF_3 *with Organic Substances Containing Nitrogen or Phosphorus*

(a) *Compounds of* BF_3 *with amines.* With BF_3 all amines form 1 : 1 coordination compounds. They are obtained by passing boron fluoride into amines dissolved in any solvent, or by treating boron fluoride etherates with the corresponding amines [102].

According to their structure the coordination compounds of boron fluoride with amines are products formed by means of a donor—acceptor linkage [103] between a nitrogen atom (donor) and a boron atom (acceptor).

Trimethylamine boron fluoride $BF_3 . N(CH_3)_3$ is prepared by the reaction [101, 107]

$$BF_3 . O(C_2H_5)_2 + N(CH_3)_3 \rightarrow BF_3 . N(CH_3)_3 + (C_2H_5)_2O$$

and when purified by repeated sublimation in a vacuum, a white crystalline substance of m. p. 146—146·5° [101] is formed. This compound, prepared by passing dry BF_3 slowly into a solution of anhydrous trimethylamine (b. p. 30—60°) in petroleum ether cooled to 0° and recrystalized from hot benzene, has m. p. 138° [102]. Burg and Green [106] isolated $BF_3 . N(CH_3)_3$, with m. p. 139—147°.

A purer product is known to be obtained by sublimation. It is stable and can be kept in a well closed bottle. An inadequately purified product, prepared by recrystallization from a solvent, gradually changes from white to light brown.

Triethylamine boron fluoride of m. p. 29·5° [104] and dimethylaniline boron fluoride of m. p. 90—92° are obtained in the same way [101].

A compound of BF_3 with dimethylamine is obtained in 90 per cent yield by passing dimethylamine into boron fluoride ethyl etherate dissolved in three parts by weight of benzene [105]. This compound does not react with triethylamine; on heating to 240—295° it forms the dimer of dimethylamine boron difluoride of m. p. 167—169° and dimethylammonium fluoroborate according to the reaction

$$4BF_3 . NH(CH_3)_2 \rightarrow 2(CH_3)_2NBF_2 + 2(CH_3)_2NH_2 . BF_4$$

Coordination compounds of BF_3 with tertiary and secondary aliphatic amines, particularly with trimethylamine and dimethylamine, are strongly associated in a non-polar solvent (benzene) [102]. The compound $BF_3 . N(CH_3)_3$ is associated (but does not dissociate) even in the vapour phase at a temperature below 230° [105].

Burg and Green [106] synthesized the compounds $BF_3 . N(CH_3)_3$, $(CH_3)_3N . B(CH_3)F_2$, $(CH_3)_3N . B(CH_3)_2F$ and $(CH_3)_3N . B(CH_3)_3$ and found that the stability of the bond between the boron and nitrogen in the specified compounds depends on the high electronegativity of the fluorine atom. Thus, trimethylamine boron fluoride is the most stable compound. By substituting the fluorine atom in this compound by methyl groups the bond between the boron and nitrogen atoms is gradually weakened, as seen from Table 22.

Table 22. B—N *bond energies in some coordination compounds* [106]

Compound	B—N bond energies (kcal)
$BF_3 . N(CH_3)_3$	30·0
$CH_3BF_2 . N(CH_3)_3$	23·1
$(CH_3)_2BF . N(CH_3)_3$	18·3
$(CH_3)_3B . N(CH_3)_3$	14·0

Primary aromatic amines, for example aniline, from coordination compounds with boron fluoride in the form of a solid, white substance, but these compounds are unstable, are easily hydrolysed by water, and attack glass [107].

When BF_3 is passed into a cooled solution of pyridine in benzene a compound $BF_3 . NC_5H_5$ [16, 108] is formed, which is one of the stable coordination compounds of boron fluoride with amines. A model of the molecule of this compound is given in Fig. 12. The product indicated is a white, crystalline substance with m. p. 45°, it distils at 300° without decomposition and dissociates at higher temperatures. Its energy of formation is 51 kcal, i. e. it corresponds to the ordinary chemical bond.

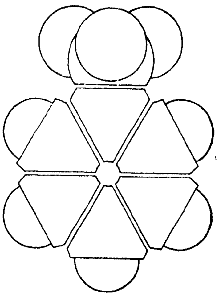
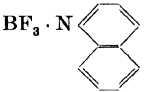


Fig. 12. Model of a molecule of pyridine-boron fluoride.

As well as this, pyridine also gives a compound $C_5H_5N \cdot 2BF_3$ which crystallizes from alcohol without decomposition.

Quinoline absorbs BF_3 forming a product [16]:



Urotropine, or hexamethylenetetramine, which has four equivalent tertiary amino nitrogen atoms capable of giving their unshared pair of electrons to four boron atoms, as might have been expected gives an addition product $(CH_2)_6N_4 \cdot 4BF_3$ in which there are 4 molecules BF_3 per 1 molecule urotropine. The compound is prepared by the addition of BF_3 to urotropine dissolved in liquid SO_2 [109], and is a white, crystalline substance of m. p. 155—160° *(in vacuo)*, which fumes in air and decomposes at 180°. In this compound the four BF_3 molecules are not equally firmly linked to the urotropine molecule. Three molecules of BF_3 split off comparatively easily at high temperature, but as soon as the cleavage reaches the formation of a compound of the approximate composition $BF_3 \cdot N_4(CH_2)_6$, the product becomes so stable that BF_3 splits off only at the decomposition temperature of urotropine.

Brown and collaborators [110] studied the reaction of BF_3 and $B(CH_3)_3$ with trimethylamine, pyridine and α, α'-lutidine and showed that trimethylamine, as a stronger base than pyridine (their ionization constants in water are $6{\cdot}3 \times 10^{-5}$ and $2{\cdot}3 \times 10^{-9}$ respectively), displaces pyridine from its compounds with the acids HCl, HBr, BF_3 because it forms more stable coordination compounds with them, than pyridine. For example in the reaction

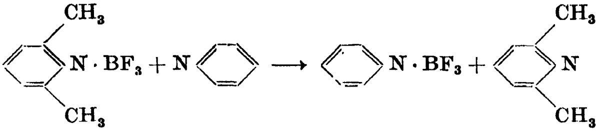
$$C_5H_5N \cdot BF_3 + N(CH_3)_3 \rightleftarrows C_5H_5N + BF_3 \cdot N(CH_3)_3$$

the equilibrium is displaced to the right by 85—90 per cent. With trimethyl boron, pyridine forms a more stable coordination compound than trimethylamine, and displaces it according to the reaction

$$(CH_3)_3N \cdot B(CH_3)_3 + C_5H_5N \rightarrow C_5H_5N \cdot B(CH_3)_3 + N(CH_3)_3$$

owing to the fact that the methyl groups create steric hindrance in the formation of a coordinate bond between the boron and the nitrogen. Therefore α, α'-lutidine, in which steric hindrance is even stronger than in trimethylamine, in general does not form a coordination compound with trimethyl boron even at a temperature of —80°.

Steric factors also explain the fact that pyridine, being a weaker base than α, α'-lutidine (their ionization constants in water are 1×10^{-7} and $2{\cdot}3 \times 10^{-5}$ respectively), nevertheless displaces it from the coordination compound with boron fluoride according to the reaction



(b) *Compounds of* BF_3 *with acid amides.* Boron fluoride with acid amides forms 1 : 1 coordination compounds in which the donor is the nitrogen atom and not the carbonyl oxygen, which results from the formation of esters from the compound $RCONH_2 . BF_3$ and alcohols.

The coordination compound $CH_3CONH_2 . BF_3$ [16] is a viscous, colourless liquid, almost without odour, which does not fume in air, and on long standing $CH_3CONH_2 . BF_3$ separates from it in the form of needle-shaped crystals. This compound is very reactive: with the alcohols CH_3OH C_2H_5OH, $(CH_3)_2CHOH$, normal and *tert.*- C_4H_9OH and C_6H_5OH it forms esters (acetates) of the corresponding alcohols in yields of 71, 69, 32, 50, 38 and 50 per cent respectively [111].

$C_6H_5NHCOCH_3 . BF_3$ is a solid crystalline product of m. p. 133°, and it readily decomposes on melting [89].

$C_6H_5N(CH_3)COCH_3 . BF_3$ is prepared [89] by running an ethereal solution of methylacetanilide into an ethereal solution of BF_3. The product recrystallized from a mixture of acetone and di*iso*propyl ether has m. p. 114°. Parachor: found 458·2, calculated 452·5.

(c) *Compounds of* BF_3 *with acid nitriles.* The nitrile group with an unshared pair of electrons on the nitrogen is a very strong donor, and therefore with substances containing such groups BF_3 forms 1 : 1 coordination compounds.

The simplest representative of this type of compound is the addition product of BF_3 to hydrocyanic acid, which is a white, solid substance of composition $BF_3 . HCN$ [112].

Acetonitrile boron fluoride $CH_3CN . BF_3$ was first briefly described by Patein in 1891 [113]. Later it was prepared by Nieuwland [16] and studied in detail by Laubengayer and collaborators [114]. Laubengayer prepared acetonitrile boron fluoride by passing gaseous BF_3 directly into liquid acetonitrile placed in a flask and isolated from the moisture of the air by a calcium chloride tube, and he thought that his product with m. p. 135·5° was purer than that isolated by Patein (m. p. 120°) and Nieuwland (m. p. 87°). The compound fumes in moist air and undergoes hydrolysis, and may be stored without decomposition in a closed vessel over phosphorus pentoxide. In the gas phase it is completely dissociated, i. e. in the vapours there exists only a mixture of CH_3CN and BF_3. The heat of formation of $CH_3CN . BF_3$ from the gaseous components is 26·5 kcal. The dipole moment is 5·8 *D*. Interatomic distances: B—F = 1·32; B—N = 1·64; N—C = 1·13 and C—C = 1·44 Å. Angles between bonds F—B—F = 114° and F—B—N = 103° [115].

Coordination compounds of boron fluoride with benzonitrile and *o*-, *m*- and *p*-tolunitriles have also been prepared [116].

It is very characteristic that in constrast to *α*, *α'*-lutidine, in the case of aryl nitriles the presence of methyl groups in the *o*-position does not create steric hindrance in the formation of coordination compounds with boron fluoride [116].

(d) *Compounds of* BF_3 *with oxides of organic amines and phosphines.* Burg and collaborators studied the coordination compounds of boron fluoride with the oxides of trimethylamine [117] and trimethyl phosphine [118] and that in both cases the BF_3 linkage was brought about at the expense of a donor — an oxygen atom (although here it resembles a carbonyl oxygen). The oxygen atom in trimethylphosphine oxide

Table 23. *Compounds of* BF_3 *with amines, amides, nitriles and other organic compounds containing nitrogen and phosphorus*

Compound	m. p. (°C)	b. p. (°C/mm)	Literature reference
$CH_3NH_2 . BF_3$	—	—	[103]
$(CH_3)_2NH . BF_3$	—	—	[105]
$(CH_3)_3N . BF_3$	146—146·5; 138; 140—146; 139—147	233	[101, 102] [105, 106]
$C_2H_5NH_2 . BF_3$	89	—	[105]
$(C_2H_5)_2NH . BF_3$	160	—	[104]
$(C_2H_5)_3N . BF_3$	29·5	—	[101]
$C_6H_5N(CH_3)_2 . BF_3$	90—92 in a sealed tube	—	[101]
$C_6H_5NH_2 . BF_3$	Readily decomposes	—	[107]
Pyridine . BF_3	45	300	[108]
Piperidine . BF_3	—	—	[16]
Quinoline . BF_3	—	—	[16]
$(CH_2)_6N_4 . BF_3$	155—160	—	[109]
$CH_3CONH_2 . BF_3$	Decomposes	—	[16]
$C_6H_5NHCOCH_3 . BF_3$	133	—	[89]
$C_6H_5N(CH_3)COCH_3BF_3$	114	—	[89]
$HCN . BF_3$	40	—	[112]
$CH_3CN . BF_3$	87, 120, 135·5	101/752	[16, 113] [114]
$C_6H_5CN . BF_3$	105—121	—	[116]
$o\text{-}CH_3C_6H_4CN . BF_3$	77—86	—	[116]
$m\text{-}CH_3C_6H_4CN . BF_3$	65—76	—	[116]
$p\text{-}CH_3C_6H_4CN . BF_3$	111—133	—	[116]
$C_6H_5CH = NC_6H_5 . BF_3$	135—145	—	[119]
$C_6H_5C(CH_3) = NOH . BF_3$	107—113	—	[16]
$(CH_3)_3NO . BF_3$	89	—	[117]
$(CH_3)_3PO . BF_3$	149	—	[118]

$(CH_3)_3PO$ is a weaker donor of electrons than the oxygen atom in trimethylamine oxide $(CH_3)_3NO$ and the coordination compound with the latter is more stable.

The coordination compound $(CH_3)_3NO . BF_3$ [117] is prepared by passing pure BF_3 into a dry chloroform solution of trimethylamine oxide. This product is a solid substance of m. p. 89° and is quite stable in air. At 100° it begins to decompose and takes on a reddish-brown colour; it partially sublimes; at 175° it becomes dark brown, and at 200° it chars completely. It dissolves in water, but more difficultly than trimethylamine oxide. An aqueous solution is not hydrolysed, and after evaporating to dryness (*in vacuo* at 60°) the original product is obtained quantitatively in the residue.

Trimethylphosphine oxide and BF_3 form a compound $BF_3 . OP(CH_3)_3$ with m. p. 149° [118], stable *in vacuo;* in water it dissolves splitting off BF_3. It is interesting to note that this oxide and sulphur trioxide give a coordination compound $(CH_3)_3PO . SO_3$, which is also less stable than the compound $(C_2H_5)_3NO . SO_3$. Sulphur dioxide reacts poorly with $(CH_3)_3PO$, but with $(CH_3)_3NO$ it forms a very stable compound $(CH_3)_3NO . SO_2$. These examples clearly show that the donor properties of the oxygen atom linked to the phosphorus are much weaker than those of the oxygen atom linked to the nitrogen. Coordination compounds of BF_3 with amines, amides, nitriles and other organic substances containing nitrogen or phosphorus are given in Table 23.

Coordination Compounds of BF_3 *with Other Organic Substances*

Coordination compounds of boron fluoride with saturated hydrocarbons and their halogen derivatives are not described in the literature. These compounds dissolve boron fluoride sparingly and are usually considered inert in relation to it. Thus, the solubility of BF_3 in *n*-pentane at 49, 66 and 93° (Fig. 13) and a pressure from 3·8 to 14·8 atm is from 1 to 12 ml BF_3 per 1 g *n*-pentane [120]. Investigation of the systems $BF_3—CH_3Cl$ $BF_3—CClF_3$ and $BF_3—CF_4$ (Figs. 14—16) by the method of thermal analysis in no case permitted the formation of chemical compounds to be established [53, 57]. A number of investigators explain such inertia by the incapability of the carbon atoms of saturated hydrocarbons, like the halogenatoms, to be donors of electrons for the boron atom.

As regards compounds of boron fluoride with unsaturated hydrocarbons, although they have not been isolated in the free state, they no doubt exist and are hypothetically assumed by all investigators to be unstable intermediate products in condensation, polymerization and other reactions in which BF_3 is used as a catalyst. In the given case the boron atom may become tetravalent negatively charged at the expense of electrons of the carbon atom linked by a double bond. For example, with ethylene it is possible to form the compound $H_2\overset{+}{C}-CH_2-\overset{-}{B}F_3$.

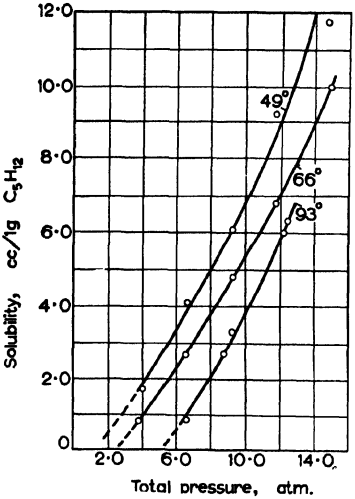


Fig. 13. Solubility of BF_3 in pentane at constant temperature. Solubility, cm³ per 1 g C_5H_{12}. Total pressure, atm.

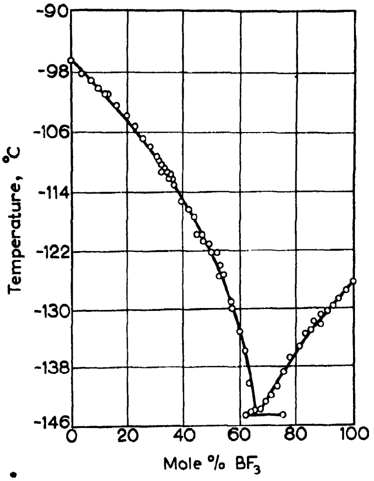


Fig. 14. The system BF_3—CH_3Cl. Temp. °C; mole % BF_3.

Thus, at present only eight elements of the periodic system of the elements are known which can form coordination compounds with the boron atom of BF_3. These elements are C (Group IV), N and P (Group V), O

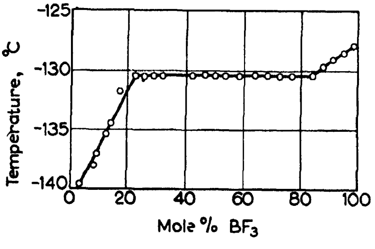


Fig. 15. The system BF_3—$CClF_3$. Temp. °C; mole % BF_3.

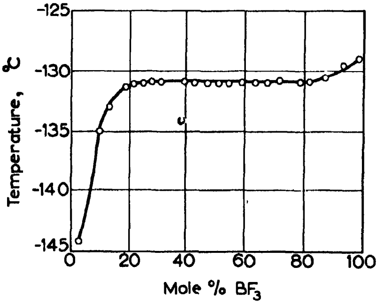


Fig. 16. The system BF_3—CF_4. Temp. °C; mole % BF_3.

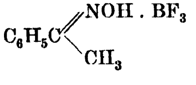
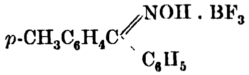
and S (Group VI), F and Cl (Group VII) and A (Group 0). They all behave as donors of electrons and form a donor-acceptor link with the boron atom of the BF_3.

As might be expected, coordination compounds of boron fluoride with substances in which atoms of elements of Groups I, II or III of the periodic system of the elements would be donors have not been described as yet.

At the present time a considerable number of coordination compounds and other halogen compounds of boron have been prepared and described [121].

A survey of the investigations on coordination compounds of all halogen compounds of boron show that the boron atom in boron fluoride has the strongest acceptor properties, and the boron atom in boron iodide has the weakest, because the electronegativity of the halogens, as is known, decreases from fluorine to iodine. Therefore the number of known coordination compounds of boron halides increases as their molecular weight decreases, i. e. from BI_3 to BF_3, as seen from Table 24.

Table 24. Coordination compounds of boron halides with amines and certain other compounds containing nitrogen [121]

BF_3	BCl_3	BBr_3	BI_3
$CH_3NH_2 . BF_3$			
$(CH_3)_3N . BF_3$	$(CH_3)_3N . BCl_3$		
$C_2H_5NH_2 . BF_3$			No compounds
$(C_2H_5)_2NH . BF_3$			
$(C_2H_5)_3N . BF_3$	$(C_2H_5)_3N . BCl_3$	$(C_2H_5)_3N . BBr_3$	
$(CH_2)_6N_4 . 4BF_3$		*iso*-$C_5H_{11}NH_2 . BBr_3$	
$C_{23}H_{26}N_2O_4 . H_2O . 2BF_3$			
$CH_3CONH_2 . BF_3$			
$C_6H_5NH_2 . BF_3$	$C_6H_5NH_2 . BCl_3$	$C_6H_5NH_2BBr_3$	
$C_6H_5N(CH_3)_2 . BF_3$	$C_6H_5N(CH_3)_2 . BCl_3$	$C_6H_5N(CH_3)_2 . BBr_3$	
p-$CH_3C_6H_4NH_2 . BF_3$	p-$CH_3C_6H_4NH_2 . BCl_3$		
$C_6H_5NHCOCH_3 . BF_3$			
$C_6H_5N(CH_3)_2COCH_3 . BF_3$		$(C_6H_5)_2NH . BBr_3$	
$C_6H_5NHNa . BF_3$			
$C_6H_5NHK . BF_3$			
$C_6H_5CH = NC_6H_5 . BF_3$			
 $C_6H_5C\begin{matrix}/\!\!/ NOH . BF_3\\ \diagdown CH_3\end{matrix}$			
 $p\text{-}CH_3C_6H_4C\begin{matrix}/\!\!/ NOH . BF_3\\ \diagdown C_6H_5\end{matrix}$			
Pyridine . BF_3		Pyridine . BBr_3	
Pyridine . $2BF_3$			
Piperidine . BF_3		Piperidine . BBr_3	
Quinoline . BF_3		Quinoline . BBr_3	

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CHAPTER IV

COMPOUNDS OF BORON WITH HYDROGEN AND THEIR PHYSICO-CHEMICAL PROPERTIES

COMPOUNDS of boron with hydrogen are prepared in a number of cases from boron halides [1, 2]. Boron hydrides (boranes) are very interesting substances which, like boron fluoride, form coordination compounds with certain organic substances as a result of additional valency forces, and also can enter directly into reaction with hydrocarbons with the formation of organoboron compounds [3].

In the Russian abstract literature little attention has been paid to inorganic compounds of boron with hydrogen and nitrogen and some of their inorganic derivatives, although B. V. Nekrasov [4], who is the author of many interesting papers on the theory of the structure of boranes, deals with this question briefly in his book.

The existence of compounds of boron with hydrogen was pointed out as long ago as 1881, but the study of boranes was held up because of the absence of the special methods of investigation which were necessary for the study of mixtures of substances very sensitive to moisture and to the oxygen of the air. Progress in this field of chemistry occurred after Stock [5, 6] had developed a special apparatus for the low-temperature vacuum distillation of boranes, which is necessary for the isolation and purification of these compounds. After this, boranes were defined as individual chemical compounds which could be represented by the formulae B_nH_{n+4} where $n = 2$, 5, 6 or 10; and B_mH_{m+6} where $m = 4$ or 5. Besides the compounds isolated and studied, mixtures of liquid and solid boranes were obtained, the composition of which has not yet been established.

Tetraborane B_4H_{10} [7] was the first of the boranes to be discovered and then other boranes. Boranes are very reactive substances, and they therefore form numerous compounds, for example with metals, metal hydrides, ammonia and many other substances, and moreover these compounds may offer no less interest than the original hydrides.

1. PHYSICAL PROPERTIES OF BORANES

Boranes are gaseous, liquid and solid compounds. Some of them are unstable in air, others are fairly stable but in comparison with hydrocarbons they are consistently more active chemically. Boranes have an

Table 25. *Properties of boranes and their derivatives* [17, 18]

Compound	Formula	m. p. (°C)	b. p. (°C)	sp. gr. (°C)	Vapour pressure, mm (°C)	General characteristics	Lit. ref.
Diborane	B_2H_6	—165·5	—92·5	0·447 (—122)	225 (—111·9)	Explodes in the presence of moisture, ignites in air, thermally unstable	[6]
Tetraborane	B_4H_{10}	—120	18	0·56 (—35)	388 (0)	Ditto	[6]
Stable pentaborane	B_5H_9	—46·6	48·6; 15·1 (131 mm)	0·630 (16)	66 (10)	Does not ignite in air at 10—20°. Decomposes very slowly with water	[8]
Unstable pentaborane	B_5H_{11}	—123	63	—	53 (0)	Ignites spontaneously in air, decomposes at room temperature	[9]
Hexaborane	B_6H_{10}	—65·1	0/7·2 mm	0·69 (0)		Does not ignite in air, decomposes slowly, is slowly hydrolysed by water	[6]
Decaborane	$B_{10}H_{14}$	99·7	213; 156/162·4 mm	0·92 (99)	19 (100)	Does not ignite, does not decompose, is slowly hydrolysed by water	[6]
Borazole	$B_3N_3H_6$	—58	55	0·8519		Chemically stable, dissolves in cold water without chemical action, is hydrolysed on heating	[10]
Diborinamide	$B_2H_5NH_2$	—66·4	76		—	Decomposes slowly	[11]
Aluminium borohydride	$Al(BH_4)_3$	—65·4	44·5	0·5588 (13·8)	119·5 (0)	Reacts vigorously with water and oxygen	[12]
Lithium borohydride	$LiBH_4$	273 with decomposition				Stable to oxygen in the absence of water	[13]
Beryllium borohydride	$Be(BH_4)_2$	31	91·3	—	5·12	Reacts vigorously with water and the oxygen of the air	[14]
Sodium borohydride	$NaBH_4$	400	—	—	—	Solid substances decompose on heating, partially sublimate *in vacuo*	[15—17]
Salts of boranes	$K_2B_2H_6$ CaB_2H_6 $Na_2B_4H_{10}$						

acid character, and therefore they form solid salt-like compounds with ammonia; on heating, these give a series of other compounds of boron with hydrogen and nitrogen, of which borazole offers the greatest interest from the theoretical point of view, being surprisingly reminiscent of benzene in structure and physical properties.

Boranes give borohydrides of metals, of which aluminium borohydride is liquid and easily distilled, and the remaining borohydrides are solid substances. With sodium, potassium and calcium, boranes give solid, stable salts, and the formation of these salts between metal and borohydride proceeds without evolution of hydrogen.

The properties of boranes and other most important compounds based on them are given in Table 25.

More detailed data about the physical properties of individual boranes are summarized in Tables 26—30.

The vapour pressure p of diborane in mm mercury, the surface tension γ in dyn/cm and the viscosity η in mP (millipoises) can be calculated from the following equations [19]:

$$\log p = 7{\cdot}185 - 782{\cdot}8/T$$
$$\gamma = (65{\cdot}7 - 0{\cdot}277\,T)\,d^{2/3}$$
$$\eta = 36{\cdot}86 \times 10^{-5}\,d^{1/3}\,e^{651{\cdot}8d/T}$$

where T is the temperature in °K, d is the density and e is the base of natural logarithms.

The critical temperature and pressure of diborane B_2H_6 are 16·7° and 40·6 atm [20]. Some physical properties of diborane are shown in Table 26.

Table 26. *Physical properties of diborane* B_2H_6 [19]

T (°K)	Vapour pressure (mm Hg)		T (°K)	Density of liquid (g/cm³)	T (°K)	Density of gas (g/cm³)
	Found	Calculated				
243·1	8890	9200	243·6	0·333	246·2	0·0382
249·9	10,800	11,300	249·9	0·316	251·3	0·0393
256·1	13,400	13,400	255·9	0·307	255·3	0·0470
268·1	19,000	18,400	268·1	0·285	260·8	0·0492
275·8	21,700	22,200	275·9	0·259	265·8	0·0541
277·3	22,400	23,000	277·8	0·253	270·7	0·0588
277·8	22,700	23,200	—	—	274·0	0·0625
284·0	26,300	26,800	284·1	0·231	285·2	0·0927
287·1	28,100	28,700	287·1	0·213	288·2	0·1100
288·9	30,200	29,800	288·4	0·154		

For calculating the boiling point of hydrocarbons and silanes, an equation of the general form:

$$T = a \log (n + b) + k$$

has recently been proposed, where T is the boiling point in °K, n is the number of central atoms, and a, b and k are constants. For silanes this equation has the following form:

$$T = 395{\cdot}8 \log (n + 3{\cdot}5) - 416{\cdot}31$$

The calculated data for disilane Si_2H_6, trisilane Si_3H_8 and tetrasilane Si_4H_{10} differ from the experimental ones only in fractions of degree. The equation was verified also for boranes, but it does not give good results on account of the complex structure of these compounds [21].

The physical properties of pentaborane are given in Table 27.

Table 27. *Physical properties of pentaborane* B_5H_9 [19]

Temperature (°K)	Density (g/cm³)	Temperature (°K)	Viscosity (m P)	Temperature (°K)	Surface tension (dyn/cm)
226·9	0·681	232·2	7·82	233·9	28·9
227·0	0·681	245·0	5·29	245·1	27·4
235·2	0·675	246·5	5·64	249·0	27·0
235·4	0·675	253·2	5·14	264·7	24·8
246·1	0·666	258·4	4·78	286·0	22·0
253·0	0·660	264·1	4·45	303·3	20·0
263·2	0·652	269·5	4·17	—	—
277·6	0·642	274·1	3·94	—	—
283·5	0·635	279·6	3·68	—	—
289·3	0·630	286·4	3·42	—	—

The density, surface tension and viscosity of pentaborane may be calculated from the equations:

$$d = 0{\cdot}8674 - 0{\cdot}00082\, T$$
$$\gamma = (71{\cdot}1 - 0{\cdot}1437\, T)\, d^{2/3}$$
$$\eta = 41{\cdot}15 \times 10^{-5}\, d^{1/3}\, e^{1024d/T},$$

The physical properties of aluminium borohydride at different temperatures are given in Table 28.

The density, surface tension and viscosity of aluminium borohydride can be calculated from the equations:

$$d = 0{\cdot}7866 - 0{\cdot}000793\, T$$
$$\gamma = (61{\cdot}0 - 0{\cdot}130\, T)\, d^{2/3}$$
$$\eta = 23 \times 10^{-3} d\, e^{1291d/T}$$

There is not enough light thrown on the thermochemical properties of boranes and borohydrides in the literature. The data published by different authors in many cases disagree. For aluminium borohydride in

Table 28. *Physical properties of aluminium borohydride* $Al(BH_4)_3$ [19]

Temperature (°K)	Density (g/cm³)	Viscosity (m P)	Temperature (°K)	Surface tension (dyn/cm)
209·3	0·6203	9·28	209·6	24·6
217·3	0·6141	7·58	216·2	23·8
228·9	0·6047	5·91	227·4	22·6
239·6	0·5966	4·69	238·3	21·3
261·7	0·5881	3·39	248·9	20·0
265·0	0·5805	3·12	258·7	19·0
274·1	0·5690	—	260·3	18·8
287·4	0·5588	2·34	263·7	18·6
306·6	0·5445	1·93	286·8	16·0
—	—	—	305·1	14·3

1946 a heat of formation of 7·2 kcal/mole was given [19], and for diborane B_2H_6 29·5 kcal/mole [2]. In 1948 the value −6·63 kcal/mole was given for the heat of formation of B_2H_6 based on the changes in heat effect of the hydrogenation of boron:

$$2\,B\ (\text{hard, amorphous}) + 3\,H_2\ (\text{gas}) \rightarrow B_2H_6\ (\text{gas}) - 6{\cdot}63\ (\pm 0{\cdot}52)\ \text{kcal/mole}$$

In this case an endothermic character is ascribed to diborane which is very probable because the pyrolysis of diborane is accompanied by the evolution of heat.

The heat of combustion of diborane [22] according to the equation

$$B_2H_6 + 3\,O_2 \rightarrow B_2O_3 + 3\,H_2O + 508{\cdot}5\ \text{kcal}$$

is determined by the heat of formation of diborane, water and boric anhydride (Table 29), but different values for the heat of formation of boric anhydride are given in the literature.

Table 29. *Heat of formation of* B_2O_3

Author	Year	Heat of formation (kcal mole)	Literature reference
Berthelot	1878	279·9	[24]
Roth	1937	349	[25]
Roth	1946	345	[22]
Todd, Miller	1946	335	[26]
Prosen *et al.*	1948	303	[23]
Eggersgluess, Monroe	1949	281·1	[27]
Johnston *et al.*	1951	302	[28]
E. V. Britske and A. F. Kapustinskii	1949	349	[29]

Such a variation in the values of the heat of formation of B_2O_3 is explained by the experimental difficulties in its determination.

For the heat of vaporization of B_2O_3 the values 65·6 kcal/mole [30] and 77·6 kcal/mole [31] are given.

Taking the heat of formation of B_2O_3 as equal to 335 kcal/mole [25], and the heat of vaporization as equal to 65·6 kcal/mole [30], higher and lower values for the heat of combustion of diborane B_2H_6 are $Q_h = 18·4$ kcal/g and $Q_l = 16·0$ kcal/g respectively, and the lower heat of combustion in the mixture $B_2H_6 + 3\ O_2$ is 3·58 kcal/g.

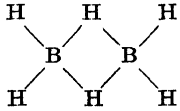
Some thermodynamic functions of decaborane are given in Table 30.

Table 30. *Thermodynamic functions of decaborane* $B_{10}H_{14}$ [32]

Temperature (°K)	Cp (cal/mole/deg)	S (cal/deg)	$H° - H_0°$ (cal/mole)	$(H°—H_0°)/T$	$(F°—H_0°)/T$
14	0·810	0·270	2·835	0·203	0·067
25	3·350	1·352	24·714	0·989	0·363
50	8·135	5·381	176·86	3·537	2·207
75	11·135	9·300	421·08	5·614	3·686
100	13·325	12·799	726·47	7·265	5·534
125	16·30	16·074	1094·8	8·758	7·316
150	20·03	19·365	1547·5	10·317	9·048
175	24·62	22·790	2104·3	12·025	10·765
200	29·82	26·414	2784·3	13·922	12·423
250	41·02	34·254	4551·3	18·205	16·049
275	47·13	38·448	5652·7	20·555	17·893
298·16	52·42	42·475	6806·9	22·830	19·645
300	52·78	42·798	6903·7	23·012	19·786

The molecular weight of decaborane is 122·31 and therefore the specific heat at 25° is equal to 0·429 cal/g. deg.

Quite a number of investigations and review articles have thrown light on the structure of boranes. The probable theory of structure was given by B. V. Nekrasov [33, 34]. According to this theory the valency structures of boron in boranes are connected among themselves by hydrogen bonds, as, for example:



Such a structure agrees with many chemical and physical properties and in particular does not contradict the results of the study of the spectra of the boranes [35].

The different theories of the structure of boranes are discussed in Bell's review [36]. Many papers have thrown light on the spectral and electronographic investigations and electron diffraction, of boranes, on the basis of which the structure of these compounds is judged [37—49].

Of the derivatives of boranes, borazole $B_3N_3H_6$ deserves special attention as it occurs among inorganic compounds as an analogue of benzene.

Borazole is a colourless, transparent, easily mobile liquid with an odour characteristic of aromatic compounds; it readily dissolves fats [10].

The density of borazole in the temperature range from −40 to + 10° can be calculated by the equation [10]

$$d = 0{\cdot}8613 - 0{\cdot}00097\,T$$

The vapour pressure of borazole at − 33° is 11·6 mm, at − 20° is 29 mm, at 0° is 85·1 mm, at 20° is 210 mm, at 40·2° is 456·2 mm and at 51·2° is 670·9 mm. It may be expressed by the equations:

$$\log p = -1565/T + 7{\cdot}6616 \quad \ldots\ldots \text{ from } -15 \text{ to } +20^\circ$$
$$\log p = -1538/T + 7{\cdot}5668 \quad \ldots\ldots \text{ from } +20 \text{ to } +50^\circ$$

where T is the temperature in °K.

The surface tension, which is 31·09 dyn/cm at −58·0° and 24·24 dyn/cm at 3·0°, may be found from the equation

$$\gamma = 24{\cdot}42 - 0{\cdot}115\,T$$

A comparison of the physical properties of borazole and benzene is given in Table 31.

Table 31. *Comparison of physical properties of borazole and benzene* [10]

Properties	$B_3N_3H_6$	C_6H_6
Molecular weight	80	78
M. p. (°K)	215	279
B. p. (°K)	328	353
Critical temperature (°K)	525	516
Density of liquid at b. p.	0·808	0·81
Heat of vaporization (kcal/mole)	7·0	7·4
Surface tension at b. p. (dyn/cm)	31·1	31·0
Parachor	208	206
Trouton constant	21·4	21·1
Interatomic distance in ring (Å)	1·44	1·39

2. CHEMICAL PROPERTIES OF BORANES

Diborane B_2H_6 is a colourless, reactive gas, readily soluble in ether and carbon disulphide, and is rapidly hydrolysed by water [6]. In the absence of moisture it does not ignite in air, but in damp air the ignition is accompanied by an explosion. It decomposes slowly on keeping, but in the pure state when stored in a sealed glass vessel the losses do not exceed 10 per cent per annum. Thus, for instance the initial product contained 99·4 per cent diborane and 0·6 per cent gas, but after six months' storage at — 18° about 2 per cent of the diborane had decomposed, because the sample contained 97·2 per cent diborane, 1·5 per cent tetraborane and 1·3 per cent gas which had not condensed at the boiling point of diborane. At a temperature of about 100° diborane decomposes with the formation of tetraborane, pentaboranes and solid products.

Tetraborane B_4H_{10} is a colourless gas, readily soluble in benzene; at room temperature it is slowly hydrolysed by water. In a sealed tube it decomposes slowly, and with increase in temperature rapid decomposition sets in with the formation of diborane, pentaborane, hydrogen and other products. Well purified tetraborane in the absence of traces of moisture evidently does not ignite in air, but in damp air it ignites spontaneously with explosion [6].

Pentaboranes B_5H_9 and B_5H_{11} are colourless liquids. Pentaborane B_5H_9 is called "stable pentaborane." Prolonged storage of B_5H_9 at room temperature for several years showed that stable pentaborane decomposes only to a negligible extent with the formation of a small quantity of hydrogen and solid residue. Slow decomposition of stable pentaborane becomes noticeable at 150°, and rapid decomposition occurs at 300°. B_5H_9 does not ignite in air, but a mixture of the vapour of pentaborane and pure oxygen ignites. This substance is hydrolysed very slowly by water (at 90° for 72 hr incomplete hydrolysis occurs). Stable pentaborane dissolves readily in the hydrocarbons *cyclo*hexane and benzene [18].

Pentaborane B_5H_{11} is called "unstable pentaborane," because it decomposes at room temperature with the formation of B_2H_6, B_4H_{10}, B_5H_9 and $B_{10}H_{14}$, and ignites spontaneously in air. It is the least stable of all the boranes that have been described. B_5H_{11} is formed in the thermal decomposition of other boranes [9].

Hexaborane B_6H_{10}.— After a prolonged time at room temperature complete decomposition of hexaborane takes place, which indicates its smaller stability in comparison with diborane. When hexaborane vapours *in vacuo* are passed through a tube heated to 300° there occurs a still incomplete decomposition of hexaborane. On dissolving B_6H_{10} in water slow hydrolysis is observed. Even on heating with water to 90° for 16 hr hydrolysis is not quite complete [6].

Decaborane $B_{10}H_{14}$ is a solid, quite stable substance, which has the greatest chemical stability in comparison with other boranes. Noticeable decomposition of $B_{10}H_{14}$ is observed only above 170°. Decaborane does not react with the oxygen of the air at room temperature, or even at 60°, but at 100° it ignites spontaneously. Decaborane is hydrolysed by water very slowly at room temperature but quickly on boiling. It dissolves readily in alcohol, ether and benzene [6].

Basic Reactions of Boranes

Boranes are halogenated like hydrocarbons:

$$B_2H_6 + Br_2 \rightarrow B_2H_5Br + HBr$$
$$B_5H_9 + Cl_2 \rightarrow B_5H_8Cl + HCl$$

when in addition to monohalogeno-derivatives higher halogen derivatives may be obtained [50]. When B_5H_9 is chlorinated, a mixture of monochloro derivatives is formed which differ in their properties and consequently are different isomers.

The halogenation of the lower boranes proceeds quietly only at low temperatures. The halogenation of decaborane, however, goes slowly at room temperature and leads to the formation of a series of halogen derivatives [50].

The reactions of diborane with boron chloride [51] and bromide [50], which lead to the formation of halogen derivatives of diborane are interesting:

$$5\,B_2H_6 + 2\,BCl_3 \rightleftarrows 6\,B_2H_5Cl \text{ chlorodiborane}$$
$$5\,B_2H_6 + 2\,BBr_3 \rightleftarrows 6\,B_2H_5Br \text{ bromodiborane}$$

Stable pentaborane and decaborane do not react with boron chloride.

The action of hydrogen halides on boranes which leads to halogenation with evolution of hydrogen is very specific. When hydrogen iodide acts directly on diborane iododiborane is formed [51]:

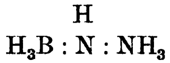
$$B_2H_6 + HI \rightarrow B_2H_5I + H_2$$

With hydrogen chloride and bromide this reaction proceeds in the presence of a catalyst, aluminium chloride or bromide [6].

Boranes react with ammonia with the formation of salt-like addition products containing a different quantity of molecules of ammonia per molecule of borane. Diborane gives the diammoniate $B_2H_6 \cdot 2\,NH_3$ [16], tetraborane gives the tetraammoniate $B_4H_{10} \cdot 4\,NH_3$ [52], and pentaborane gives the diammoniate $B_5H_9 \cdot 2\,NH_3$ and the tetraammoniate $B_5H_9 \cdot 4\,NH_3$ [52]. Unstable pentaborane also gives the tetraammoniate $B_5H_{11} \cdot 4\,NH_3$ [16]. Decaborane forms the hexaammoniate $B_{10}H_{14} \cdot 6\,NH_3$, which easily decomposes into the original substances [52]. The formation of ammoniates takes place at low temperatures (— 120°).

Borane ammoniates may be related to compounds of the ammonium salt type. The structure $NH_4^+[H_3\overset{-}{B}—\overset{+}{N}H_2—\overset{-}{B}H_3]^-$, is attributed to diborane diammoniate, corresponding to the ammonium salt of diborinamide [53]. It is considered that for the diammoniate the formula of the diammonium salt $NH_4^+{}^-[H_2B : BH_2]^-NH_4{}^+$ is less substantiated [54].

When ammonia and diborane react in equimolecular quantities with the evolution of hydrogen, diborinamide $B_2H_5NH_2$ is formed, which by its chemical nature is an amide [16]. Investigation of this compound by the method of electron diffraction indicates a symmetrical structure with the bonds B—N—B:



$$H_3B : \overset{H}{N} : NH_3$$

On storing for a long time, diborinamide slowly decomposes with the formation of diborane and solid products. It adds one molecule of ammonia and amines, and easily hydrolyses in a solution of hydrochloric acid.

When two molecules of methylamine react with one molecule of diborane a compound is obtained which is liquid at room temperature (in contrast to the diammoniate) [55]. This product on heating is converted into N-methyl borazole in good yield.

Dimethylamine reacts with diborane with the formation of "inorganic *iso*butylene" [56]:

$$B_2H_6 + 2NH(CH_3)_2 \rightarrow 2\ H_3B : NH(CH_3)_2 \rightarrow H_2B = N(CH_3)_2 + 2\ H_2$$

Diborane reacts quantitatively at − 110° with trimethylamine with the formation of trimethylamine borine:

$$B_2H_6 + N(CH_3)_3 \rightarrow 2H_3\overset{-}{B}-\overset{+}{N}(CH_3)_3$$

This product is a white, solid sublimable substance [57].

The compounds indicated are also obtained by the direct reaction of amine hydrochlorides with lithium borohydride in a medium of ether [58, 59] in a yield of 60—90 per cent according to the reaction

$$(CH_3)_2NH\ .\ HCl + LiBH_4 \rightarrow (CH_3)_2N-BH_2 + LiCl + 2H_2$$

$$(CH_3)_3N\ .\ HCl + LiBH_4 \rightarrow (CH_3)_3\overset{+}{N}-\overset{-}{B}H_3 + LiCl + H_2$$

Trimethyl borazole is obtained with the salt of a primary amine, but when a borohydride reacts with a quaternary ammonium salt a tetraalkylammonium borohydride is formed:

$$R_4NCl + NaBH_4 \rightarrow R_4NBH_4 + NaCl$$

Diborane reacts with hydrazine [60], as also with other substances of a basic character. The formation of two compounds may hereby be expected:

$$H_3B : NH_2-NH_2 \text{ and } H_3B : NH_2-NH_2 : BH_3$$

B, 36·7 per cent; N, 46·8 per cent; H, 16·5 per cent; B, 24 per cent; N, 61 per cent; H, 15 per cent

When an excess of diborane reacted with hydrazine at 0° for 30 hr a white solid, hygroscopic substance having the composition B, 32·6 per cent; N, 52·0 per cent and H, 14·4 per cent, i. e. corresponding to an empirical formula $BN_{1.2}H_{4.8}$, was obtained.

Alongside the formation of the solid product hydrogen is evolved; the solid substance formed is non-volatile and does not dissolve in the usual solvents such as ether, benzene, acetone, carbon tetrachloride or ethyl acetate, and is also insoluble in hydrazine and liquid ammonia. On heating in air it explodes. As a result of the reaction between hydrazine and diborane, a mixture of both the theoretically possible products is probably obtained.

When the solid product of the reaction of diborane with hydrazine *in vacuo* is heated to 180—200° for 2—3 hr, hydrogen is liberated and a solid residue is formed.

From the product $BN_{1.26}H_{4.92}$ taken for heat treatment, a solid substance $BN_{1.26}H_{2.81}$ containing a smaller quantity of hydrogen was obtained [60].

Stable pentaborane reacts with trimethylamine forming a compound $B_5H_9 . 2N(CH_3)_3$ which on heating gives trimethylamine borane and by-products.

Diborane reacts with carbon monoxide under pressure at 100° with the formation of carbonyl borine:

$$2CO + B_2H_6 \rightleftarrows 2H_3B . CO$$

The reaction proceeds with good yield under a pressure of 20 atm [57]. Carbonyl borine is a gaseous substance melting at $-64°$ and boiling at $-37°$. At low temperatures diborane and ether form an unstable compound, dimethylborine ether $(CH_3)_2O . BH_3$, which readily decomposes [53].

Diborane reacts slowly with two molecules of phosphine in the gas phase at $-110°$ with the formation of borine phosphine, which ignites spontaneously in air and is rapidly hydrolysed by water with the formation of phosphine, boric acid and hydrogen.

Diborane reacts vigorously with pyridine [61], forming a compound $C_5H_5N . BH_3$ evidently analogous to trimethylborine amine.

The reactions of diborane with hydrocarbons, whereby organoboron compounds are obtained, are interesting [62].

Thus, when *iso*butylene was heated with diborane at 100° for 24 hr tertiary tributylboron of b.p. 181·5° and tri*iso*butyl boron of b.p. 18·5° were obtained. On heating ethylene with 2 per cent of diborane at 100° for 4 days triethylboron was obtained:

$$B_2H_6 + 6C_2H_4 \rightarrow 2B(C_2H_5)_3$$

In this case the BH_3 radicals add to three double bonds with the formation of trialkyl derivatives. At lower temperatures, however, the alkylation of B_2H_6 takes place with the formation of alkyl derivatives of diborane.

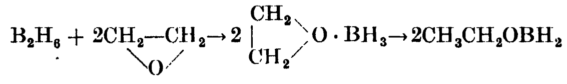
When B_2H_6 reacts with paraffin hydrocarbons, for example with C_5H_{12}, different organoboron compounds are also formed [62].

Many ketones and aldehydes, for example acetone and acetaldehyde, react with diborane forming stable addition products [63].

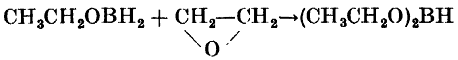
With alcohols borine derivatives are formed [64]:

$$4CH_3OH + B_2H_6 \rightarrow 2BH(OCH_3)_2 + 4H_2$$

Diborane reacts easily with ethylene oxide at −80°, forming diethoxyborane and a solid polymer containing boron. Diethoxyborane is obtained by the reaction



$$B_2H_6 + 2\underset{\diagdown O \diagup}{CH_2{-}CH_2} \rightarrow 2\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O\cdot BH_3 \rightarrow 2CH_3CH_2OBH_2$$



$$CH_3CH_2OBH_2 + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \rightarrow (CH_3CH_2O)_2BH$$

B_2H_6 reacts with propylene oxide in a similar way [65].

Although stable pentaborane does not ignite spontaneously in air at room temperature, its vapours react with pure oxygen with explosion. In 1951 a special paper [66] was written on the kinetics of this process. The low limiting concentration depends on the pressure at which the $B_5H_9-O_2$ mixture exists, and on the volume of the vessel. Explosion of the $B_5H_9-O_2$ mixture at room temperature was observed with a total pressure in the system of 3—6 mm, but the formation of the explosion

Table 32. *Conditions of explosion of the system* $B_5H_9-O_2$ *in a spherical quartz vessel at room temperature* [66]

	Diameter of vessel 3·7 cm							
Vapour pressure of B_5H_9 (mm)	0·77	0·83	4·45	4·36	1·00	1·74	1·57	
Pressure of O_2 (mm)	2·9	2·8	1·9	2·1	2·7	2·2	2·4	
Result*	Exp.	No	No	Exp.	No	No	No	
	Diameter of vessel 6·62 cm							
Vapour pressure of B_5H_9 (mm)	1·03	1·01	1·98	1·94	2·98	3·01	4·02	4·08
Pressure of O_2 (mm)	1·5	1·66	1·32	1·33	1·18	1·25	1·13	1·19
Result*	No	Exp.	No	Exp.	No	Exp.	No	Exp.

* Exp. — explosion occurred; No — explosion did not occur.

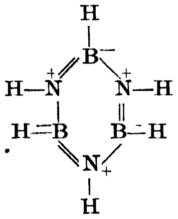
depends on the composition of the combustible mixture and the volume of the vessel (Table 32).

Cool flame oxidation has also been investigated in the system $B_5H_9—O_2$ [66].

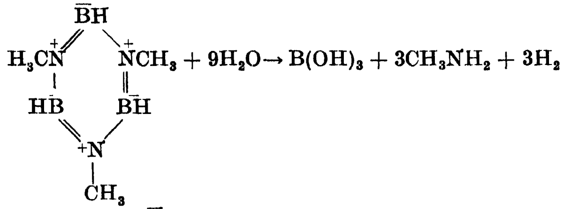
Borazole

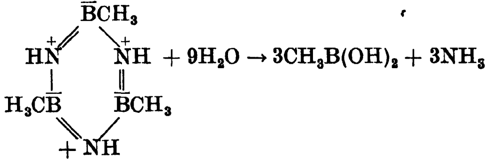
Borazole was discovered in 1926 by Stock and Pohland [17]. From a chemical point of view borazole is a cyclic aminoborohydride. On a basis of the chemical and physical properties and the study of electron diffraction a cyclic formula with three boron and three nitrogen atoms in the ring is given to it [67, 68] and the length of the B—N bond is 1·44 Å.

The homopolar bonds between the nitrogen and boron atoms in the ring are supplemented by ionic bonds:



The structure of borazole may be demonstrated by the hydrolysis of it trialkyl-substituted on the nitrogen (1) and the boron (2):


(1)


(2)

The formation of three molecules of methylamine in the first case and of three molecules of methyl boric acid in the second is possible only when each atom of nitrogen and boron is joined to a methyl group, and in the original compound, to the hydrogen atoms.

According to its physical properties, infra-red spectra and Raman spectra, borazole is close to benzene (see above, Table 31). In comparison with boranes, borazole is a very stable compound, but is considerably more reactive than benzene. Thus, it does not decompose on heating to 500°, but at room temperature it gradually polymerizes with the formation of products of the "polyphenyl" type with a long chain, in which B—N bonds are formed between residues of borazole molecules with loss of hydrogen. Opinions about the stability of borazole are exaggerated, because hydrohalic acids, water, alcohols, ethers and even ammonia add to it. In most cases it adds three molecules of corresponding substances.

With water at 0° the trihydrate is formed:

$$B_3N_3H_6 + 3H_2O \rightarrow B_3N_3H_6 . 3H_2O$$

Molecules of alcohols are also added in threes:

$$B_3N_3H_6 + 3ROH \rightarrow B_3N_3H_6 . 3ROH$$

The addition of hydrohalic acids to borazole proceeds slowly and requires several hours:

$$B_3N_3H_6 + 3HX \rightarrow B_3N_3H_6 . 3HX$$

The addition product of hydrobromic acid splits off hydrogen with the formation of tribromoborazole on heating to 50—100°:

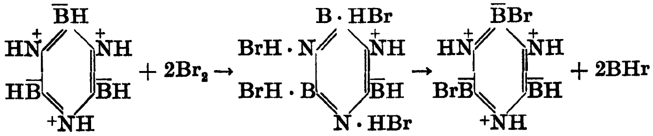
$$B_3N_3H_6 . 3HBr \rightarrow B_3N_3H_3Br_3 + 3H_2$$

Ammonia reacts with borazole with difficulty, and in several days only two molecules of ammonia are added.

In view of the slowness of additions to borazole Wiberg [69] considers that they are not of a coordinating character but that the addition takes place on the double bonds which are supposed to be in borazole.

From our point of view, this suggestion seems highly improbable because the addition is rather of a coordinating character, but it is slowed down owing to the fact that the boron and nitrogen atoms are already coordinated with each other in the ring. The addition of oxygen compounds occurs on the boron atom and of hydrohalic acids on the nitrogen atom, but with preliminary disruption of the coordinate bonds in the ring.

When bromine acts on borazole at room temperature an addition product of two molecules of bromine is formed, which decomposes on heating to 60—70° into dibromoborazole and hydrogen bromide [69]:



In dibromoborazole the bromine is linked to the boron atoms, and this compound hydrolyses easily with the formation of dihydroxyborazole.

Borazole gives halogen derivatives when treated with ammonium chloride [70]. On heating 0·58 g NH_4Cl with 37·5 ml $B_3N_3H_6$ for 20 min at a temperature of 275° monochloroborazole is formed in about 5 per cent yield, and at the same time the reaction is accompanied by the evolution of hydrogen.

Halogen derivatives of borazole are obtained by treating borazole with boron chloride BCl_3 and boron bromide BBr_3. From 82·3 ml $B_3N_3H_6$ and 23·8 ml BCl_3 kept at room temperature for 116 hr 19·6 ml monochloroborazole and a little dichloroborazole were obtained, and at the same time a certain amount of hydrogen and diborane were formed.

The properties of the halogen derivatives of borazole are given in Table 33.

Table 33. *Properties of halogen derivatives of borazole* [70]

Compound	m. p. (°C)	b. p. (°C)	Trouton constant
$B_3N_3H_5Cl$	—34·6	109·5	22
$B_3N_3H_5Br$	—34·8	122·3	25
$B_3N_3H_4Cl_2$	—	151·9	21
$B_3N_3H_4Br_2$	—	167·1	29

The relationship between the vapour pressure of monochloroborazole $B_3N_3H_5Cl$ and temperature is as follows:

T (°K)	273·2	282·7	298·7	320·2
Vapour pressure (mm)	8·8	14·9	33·3	86·7

The heat of reaction in the hydrolysis of B-trichloroborazole with the formation of boric acid and ammonium chloride is 113·8 + 0·7 kcal/mole; on a basis of this the heat of formation of crystalline B-trichloroborazole was calculated, and proved to be 252·2 kcal/mole [71].

Attempts to hydrogenate borazole with platinum and other catalysts lead to disruption of the molecule [72].

Borohydrides of Metals and Salts of Boranes

An extremely interesting result of the investigations in the field of boranes is the discovery of compounds of metal-boranes of the type $Me^{I}BH_4$, $Me^{II}(BH_4)_2$, etc.

Many borohydrides of metals distil without decomposition or readily sublime and in this way can be separated in the pure state. They are used as reducing agents and are a source of production of hydrogen.

The borohydrides of lithium, beryllium, aluminium and certain other metals have been well studied [13, 14]. Lithium borohydride has a clearly defined salt-like ionic character and is stable in an atmosphere of dry air; in contrast to this, aluminium and beryllium borohydrides ignite vigorously in air, and their ionic character is weakly defined. All these compounds are easily hydrolysed by water with evolution of hydrogen, and add one molecule of trimethylamine.

The properties of many other borohydrides, $NaBH_4$, $Th(BH_4)_4$, $Hf(BH_4)_4$, $V(BH_4)_3$, $Zr(BH_4)_4$, $Ti(BH_4)_4$ have recently been described [73].

The borane salts, $Na_2B_2H_6$, $K_2B_2H_6$, CaB_2H_6 are stable compounds. The first two salts may be sublimed *in vacuo* without complete decomposition. These substances are stable in dry air, but are easily hydrolysed by water [15, 16]. Tetraborane and pentaborane give salts of alkali metals of the type $Me_2B_4H_{10}$ [15, 74] and $Me_2B_5H_9$ [15].

3. METHODS OF PREPARATION OF BORANES

Decomposition of Magnesium Boride with Acids

Boranes are obtained by the action of hydrochloric acid on magnesium boride Mg_3B_2 [7]. With this first method, proposed in 1912, there was no possibility of obtaining any considerable quantities of boranes, because the yield did not exceed 3 per cent. Later the given method was improved by replacing hydrochloric acid by phosphoric, but even in this case the yield did not exceed 10 per cent [75]. Intensive development of the chemistry of boranes was begun after the development of more perfect methods for the preparation of boranes, and at the present time according to information from the press industrial methods for their manufacture are being worked out by Schlesinger [76]. The most important of these boranes is diborane B_2H_6, because a series of other boranes and their derivatives may be obtained from it.

Reduction of Boron Halides

The preparation of diborane and boron hydrides in considerable quantities became practicable after the discovery [64, 77, 78] of the reaction of boron halides with metal hydrides and lithium aluminium hydride in absolute ether.

$$4LiH + BF_3 \rightarrow LiBH_4 + 3LiF$$
$$3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF$$
$$3LiAlH_4 + 4BF_3 \rightarrow B_2H_6 + 3AlF_3 + 3LiF$$
$$4LiAlH_4 + 4BF_3 \rightarrow Al(BH_4)_3 + LiBH_4 + 3AlF_3 + 3LiF$$
$$3NaBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3NaBF_4$$

Lithium hydride is prepared by passing hydrogen over fused lithium, and lithium aluminium hydride is obtained from LiH and $AlCl_3$ according to the reaction

$$8LiH + 2AlCl_3 \rightarrow LiAlH_4 + 6LiCl$$

Instead of gaseous boron fluoride it was suggested that its liquid ethyl etherate $(C_2H_5)_2O \cdot BF_3$ should be used. The reaction between $LiAlH_4$ and $(C_2H_5)_2O \cdot BF_3$ is conducted in a medium of ether at a temperature from 0 to 35°. In the reaction between 20·78 g $(C_2H_5)_2O \cdot BF_3$ in 80 ml ether with a varying quantity of lithium aluminium hydride solution (concentration 5·57 g $LiAlH_4$ in 100 ml ether), the results given in Table 34 were obtained [79].

Table 34

Volume of solution of $LiAlH_4$ (ml)	Molar ratio $LiAlH_4/BF_3$	Volume of B_2H_6 obtained (ml)
25·0	0·251	272·2
45·0	0·451	751·3
65·0	0·652	931·6
75·0	0·752	1096·2
85·0	0·852	1100·3

Almost quantitative (yield about 90 per cent) conversion of boronfluoride into B_2H_6 is observed in the following ratio of the reagents, which is close to the theoretical: 4·5—5·0 mole BF_3 to 3 moles $LiAlH_4$.

As a source of boron fluoride lithium fluoroborate may be used. In this case the reaction proceeds according to the equation

$$3LiAlH_4 + 4LiBF_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

Better results are obtained with the theoretical ratio of the quantities of reagents and when the reaction mixture is heated to about 350°. In this case the yield of B_2H_6 reaches 45 per cent.

The most efficient methods of preparing diborane are based on the reduction of boron halides, and therefore for the preparation of diborane in large quantities it would be more reasonable to use hydrogen directly.

A method of direct hydrogenation of boron chloride and bromide with hydrogen in a powerful electric discharge has been worked out [50]. Hydrogen is passed through liquid boron chloride at —40°, forming a gaseous mixture of $BCl_3 + H_2$ which at reduced pressure (10 mm) passes through the zone of the electric discharge (voltage 12—15 kV). The mixture obtained, consisting of H_2, HCl, BCl_3, B_2H_5Cl and boranes, is subjected to condensation to separate the hydrogen and is distilled at a pressure of 2 atm.

On distillation chlorodiborane B_2H_5Cl decomposes into diborane and boron chloride. The fractions enriched with boranes are distilled a second time. Instead of boron chloride, boron bromide may be used with good results. The yield of diborane per reacted boron chloride may reach 60—75 per cent, and the yield per boron bromide may reach 80 per cent. With regard to the ratio of the reagents and the period for which the mixture remains in the zone of the discharge different quantities of other boranes are formed.

At the present time a simpler method for the preparation of boranes based on the direct reduction of boron chloride or bromide by hydrogen in the presence of granulated aluminium or other metals linking chlorine and bromine has been developed [77].

The formation of diborane proceeds according to the equation

$$2BCl_3 + 3H_2 + 2Al \rightarrow B_2H_6 + 2AlCl_3$$

In this method a mixture of the vapours of boron chloride and hydrogen in molar ratio $BCl_3 : H_2 = 1 : 3$ is passed through a heated column, a reaction vessel of Pyrex glass filled with granulated aluminium of grain size 20 mesh. The temperature in the reaction vessel is kept within the limits 320—500°. After a short induction period the reaction begins and boranes appear in the gases. The reaction products are condensed in three receivers. In the first receiver aluminium chloride collects, and in the second at 80° the main quantity of diborane together with chlorodiborane B_2H_5Cl and the boron chloride which has not entered into the reaction. In the third receiver at —190° there also collects a certain amount of diborane and hydrogen chloride. Diborane is liberated from the mixture by fractionation.

Boron chloride does not enter completely into the reaction; depending on the conditions its conversion amounts to 6—30 per cent. The B_2H_6 content of the condensed products is 3—17 per cent. The dependence of the yield of diborane on the reaction conditions is given in Table 35.

The greatest conversion of boron chloride to diborane corresponds to a temperature of 450° and a molar ratio $BCl_3 : H_2 = 1 : 6$.

At a temperature below 300° boranes are not formed. A negligible quantity of boron chloride is converted during the reaction into the element boron which separates in the reaction vessel. Analysis of different samples of aluminium powder showed that as the surface of the metal increases the conversion of BCl_3 increases.

The preparation of diborane from BCl_3 and H_2 was also carried out over other reactive metals: over sodium, zinc and magnesium. Magnesium gave the worse result compared with aluminium.

Table 35. *Yield of diborane and conversion of boron chloride in relation to reaction conditions* [77]

Temperature (°C)	Molar ratio $BCl_3 : H_2$	Time of contact (min)	Composition of condensate (%)			Conversion of BCl_3 (%)
			B_2H_6	HCl	BCl_3	
360	1 : 4	5	2·9	4·1	93	6
320	1 : 3	12	3·5	1·3	95·2	6·7
380	1 : 3	12	5·8	0	94·2	11
350	1 : 6	15	8·8	1·7	89·5	16·4
475	1 : 6	6	12·4	1·7	85·9	20·4
500	1 : 6	4	6·7	0·9	92·4	12·5
450	1 : 6	6	17·2	3·9	78·9	30

Methods for the preparation of boron halides have been worked out [80]. Thus, boron chloride is obtained by allowing potassium fluoroborate to react with aluminium chloride [81]:

$$KBF_4 + AlCl_3 \rightarrow BCl_3 + AlF_3 + KF$$

The best yield (about 80 per cent) is, however, obtained by passing BF_3 through a vessel with heated aluminium chloride:

$$AlCl_3 + BF_3 \rightarrow BCl_3 + AlF_3$$

Boron fluoride is an industrial product which since 1936 has been obtained [82] according to the reaction

$$Na_2O \, . \, 4BF_3 + H_2SO_4 \rightarrow 4BF_3 + Na_2SO_4 + H_2O$$

and also by other methods (see above, Chapter I).

The $Na_2O \, . \, 4BF_3$ complex necessary for the reaction is prepared by treating borax with hydrogen fluoride.

Boron fluoride is a more accessible substance than the other boron halides, but its direct reduction by the method indicated above gives smaller yields of diborane than the reduction of boron chloride.

Thermal Decomposition of Diborane with the Formation of Higher Boranes

In 1936 a detailed paper [83] on the pyrolysis of diborane with the formation of higher boranes appeared. Depending on the conditions, diborane may give as main products stable or unstable pentaborane, solid boranes and also tetraborane.

The pyrolysis was carried out in a circulating apparatus at a temperature of 175—200°, the time of contact of the diborane with the heated reaction vessel being 2·7—3·3 sec and the pressure 102—106 mm. Since the conversion of diborane in one operation was small, the unreacted diborane was recirculated and the whole experiment lasted 16—20 hr.

The influence of temperature and time of contact was studied. In some cases the diborane was diluted with hydrogen or nitrogen. The effect of gases with which the diborane was diluted is given in Table 36.

Table 36. ***Effect of hydrogen and nitrogen on the conversion of diborane on pyrolysis*** [83]

Ratio		Temperature (°C)	Conversion of diborane (%)	Composition of reaction products, (mole %)			
$H_2 : B_2H_6$	$N_2 : B_2H_6$			B_4H_{10}	B_5H_9	B_5H_{11}	Solid products
0	0	174	70·9	4	3	85	8
0	0	200	92·4	4	43	39	14
0	0	225	95·6	3	63	3	31
1·0	0	200	88·6	3	40	50	7
1·0	0	225	93·0	0	81	0	19
5·0	0	175	23·3	4	0	88	8
5·0	0	200	57·3	5	28	62	5
5·0	0	225	79·0	1	78	10	11
5·0	0	225	83·3	4	82	0	17
4·9	0	225	82·1	0	86	0	14
4·9	0	225	98·7	0	37	0	63
0	5·0	185	52·9	12	0	77	0
0	5·0	211—216	88·3	3	33	47	17
0	5·0	225—227	94	5	58	7	30

The best yield of stable pentaborane B_5H_9 (about 80 per cent) was obtained at a temperature of 225°, and at the same temperature a high conversion of diborane was observed. At a lower temperature (for example, 175°) unstable pentaborane B_5H_{11} is formed in a large quantity.

The use of hydrogen in pyrolysis favours an increase in yield of B_5H_9 and a decrease in the yield of solid boranes. Dilution with nitrogen does not give good results. Increasing the reaction temperature to 250° favours an increase in the yield of solid boranes to 30—50 per cent.

The effect of the time of contact of the diborane with the heated reaction vessel on the conversion and yield of the reaction products is shown in Table 37.

The conversion of diborane depends (other conditions being equal) only on the total time it is in contact with the reaction vessel in several operations. An increase in the total time of contact favours an increase in yield of stable pentaborane B_5H_9 and of solid boranes. Additions of hydrogen chloride and bromide and of boron halides do not have any substantial effect on the reaction.

The pyrolysis of diborane is an exothermic reaction, because the temperature on reaction can increase spontaneously even when the electrical heating is discontinued.

Table 37. Effect of time of contact on the conversion and yield of boranes on pyrolysis of diborane

Ratio $H_2 : B_2H_6$	Temperature (°C)	Time of contact (sec)	Number of operations	Conversion (%)	Composition of reaction products (mole %)			
					B_4H_{10}	B_5H_9	B_5H_{11}	Solid products
0	175	3·3	150	70·9	4	3	85	8
0	175	20·8	24·1	66·6	4	18	67	11
5·0	200	3·2	15	57·3	5	28	62	5
4·9	200	6·8	105	70·7	6	56	33	5
4·9	225	3·0	169	82·1	0	86	0	14
4·9	225	13·0	36·4	87·4	0	78	0	22
1·0	228	3·0	9·4	72·1	2	55	32	11
1·0	222	6·7	4·1	69·5	2	62	17	19

In the literature it is pointed out that tetraborane is prepared by heating a 10 : 1 mixture of hydrogen and unstable pentaborane at 100° for 10 min. The main reaction proceeds according to the equation

$$2B_5H_{11} + H_2 \rightarrow 2B_4H_{10} + B_2H_6$$

The yield is about 85 per cent [9].

It is pointed out [57], that tetraborane is prepared by passing diborane through a furnace heated to 180°, and then through a trap cooled to −115° to condense the reaction products and the diborane which has not entered into the reaction. The diborane is then separated by low-temperature fractionation.

It has been suggested that pentaboranes be prepared by passing diborane through a tube at a temperature of 250° under a pressure of 120 mm at a rate of 50 ml/min; B_5H_9 is obtained in 56 per cent yield, and B_5H_{11} in 26 per cent yield [84].

Heating diborane without circulation in a closed vessel [9] gives a worse yield of pentaborane (about 30 per cent).

Unstable pentaborane B_5H_{11} is obtained in better yield when diborane B_2H_6 is passed through a tube heated to 115° at such a rate that the time of contact is 2 min. The diborane which does not enter into the reaction is separated and introduced into the reaction again. The conversion of diborane in one cycle is small, but on recirculation the yield amounts to about 90 per cent [9, 85].

Decaborane $B_{10}H_{14}$ is prepared by heating diborane at a temperature of 250°. When diborane is heated in a closed vessel at 160° and at a pressure slightly above atmospheric, the yield of decaborane $B_{10}H_{14}$ is about 30 per cent [86].

In addition to the development of methods of preparing boranes by the pyrolysis of diborane, the kinetics and the mechanism of this reaction were studied.

In 1951 the following scheme was proposed for the conversion of diborane into pentaborane [87]:

$$B_2H_6 \rightleftarrows 2BH_3$$

$$B_2H_6 + BH_3 \rightarrow B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \rightarrow B_5H_{11} + H_2$$

$$B_5H_{11} \begin{array}{l} \nearrow B_5H_9 + H_2 \\ \searrow B_2H_6 + \text{higher boranes} \end{array}$$

In the first stage of the reaction diborane dissociates into unstable borane which in the second stage, reacting with diborane, gives a hypothetical triborane, and the latter with diborane forms unstable pentaborane, from which stable pentaborane and decomposition products are obtained.

The kinetics of the pyrolysis of B_2H_6 were studied at a temperature of 85—163° and a pressure of 25—200 mm.

In another paper [85] the kinetics of the pyrolysis of B_2H_6 were studied at constant volume in a vessel of Pyrex glass.

The rate of decomposition of diborane on pyrolysis in relation to its concentration and temperature is given in Table 38. Besides the total pressure, the partial pressure of hydrogen was also measured, for which purpose the other reaction products were removed by freezing.

Table 38. *Rate of pyrolysis of diborane in a closed vessel*
(Volume 211·8 ml) [85]

Temperature of reaction (°C)	Concentration of B_2H_6 (mole/l.) $\times 10^{-2}$	Rate of increase of pressure (mole/l./hr) $\times 10^4$	Temperature of reaction (°C)	Concentration of B_2H_6 (mole/l.) $\times 10^{-2}$	Rate of increase of pressure (mole/l./hr) $\times 10^4$
89·6	2·718	3·8	110·1	2·036	19·3
89·6	2·092	2·7	110·1	1·275	9·3
89·6	1·536	1·6	110·1	0·4334	1·9
100·0	2·153	7·4	120·1	0·6332	7·1
100·0	2·188	8·0	120·1	0·4191	3·1
99·9	2·097	7·3	120·1	0·2165	1·1
99·9	1·310	3·7	130·1	0·4008	9·5
99·9	1·281	3·5	130·1	0·2119	2·9
100·0	0·437	0·73			

The rate of increase of pressure w_p on the pyrolysis of B_2H_6 is determined by the equation

$$w_p = KC_0^n$$

where C_0 is the initial concentration of diborane, n is the order of the reaction equal to 1·49 at a temperature of 89·6—110°, K is the velocity constant of the reaction which varies from 0·085 to 0·66 in the temperature range indicated.

With rise of temperature the order of the reaction increases, reaching 1·89 at 130·1°. The energy of activation of the pyrolysis of B_2H_6, found from the change of velocity constant of the reaction with a rise of temperature from 120·1 to 130·1°, is 27·4 ± 0·7 kcal/mole.

The rate of formation of hydrogen in the pyrolysis of B_2H_6 obeys a similar law: the average value of the exponent n is 1·5, and the energy of activation of the formation of hydrogen on pyrolysis is 25·5 ± 0·5 kcal/mole.

4. METHODS OF PREPARATION OF DERIVATIVES OF BORANES

Diborinamide

Diborinamide is a mobile liquid which slowly decomposes on keeping. It is obtained by passing diborane over diborane diammoniate at 88° [11]:

$$B_2H_6 \cdot 2NH_3 + B_2H_6 \rightarrow 2B_2H_5NH_2 + 2H_2$$

Diborinamide is also formed as a by-product in the preparation of borazole [16, 55]. In the study of this substance by means of electron diffraction it was shown that in its crystalline structure it approximates to dimethylamine, being by its chemical properties an amide in which two acid borine groups BH_3 are combined with the >NH group.

Diborinamide can add one molecule of ammonia, forming an ammoniate:

$$B_2H_5NH_2 + NH_3 \rightarrow NH_3 \cdot B_2H_5NH_2$$

This substance differs from diborane diammoniate $B_2H_6 \cdot 2NH_3$ in the hydrogen content and obviously in its structure. However, when heated quickly to 200° diborinamide ammoniate, like $B_2H_6 \cdot 2NH_3$, gives borazole in 45 per cent yield.

Borazole

Borazole $B_3N_3H_6$ is obtained [62] when diborane or tetraborane ammoniates are heated in a closed vessel at 180—190°:

$$3B_2H_6 \cdot 2NH_3 \rightarrow 2B_3N_3H_6 + 12\ H_2$$
$$3B_4H_{10} \cdot 4NH_3 \rightarrow 4B_3N_3H_6 + 21\ H_2$$

The preparation of borazole may be carried out directly from di- and tetraboranes and ammonia, taken in proportions corresponding to the appropriate ammoniates.

The formation of borazole from ammoniates of boranes is accompanied by side reactions which lower the yield and lead to the formation of side products. The formation of borazole may be represented by the equation

$$3B_2H_6 + 6NH_3 \xrightarrow[2-3\text{ hr}]{180^\circ} 0{\cdot}67\ B_3N_3H_6 + 14{\cdot}6H_2 + 4{\cdot}05BNH_{1{\cdot}13}$$

where, in addition to $B_3N_3H_6$, a white solid substance of composition $BNH_{1{\cdot}13}$ and hydrogen are obtained.

At a lower temperature of decomposition (e.g. 150°) 17 per cent of the diborane is converted into borazole, and 83 per cent of it into a white, solid, non-volatile product of composition $BNH_{3{\cdot}66}$, richer in hydrogen than borazole [69]. The reaction may be represented by the equation

$$3B_2H_6 + 6NH_3 \xrightarrow[2-3\text{ hr}]{150^\circ} 0{\cdot}34B_3N_3H_6 + 7{\cdot}8H_2 + 5BNH_{3{\cdot}66}$$

The yield of borazole is doubled if the reaction is carried out at 180—190° for 2—3 hr. The same yield of borazole is obtained when the time of the reaction is 15 min, but at the same time the amount of hydrogen formed changes and so does the composition of the solid phase, which may be represented by the equation

$$3B_2H_6 + 6NH_3 \xrightarrow[15\text{ min}]{180^\circ} 0{\cdot}64B_3N_3H_6 + 6{\cdot}95H_2 + 4{\cdot}07BNH_{4{\cdot}19}$$

On heating diborane with ammonia at 200—220° for 45 min the maximum yield of borazole reaches 41 per cent. A necessary condition of a good yield is the rapid bringing of the reaction products to the best temperature.

The effect of different factors on the yield of borazole is shown in Table 39.

Table 39. *Effect of reaction conditions on yield of borazole* [69]

Pressure (atm)	Temperature of reaction (°C)	Time of reaction	Molar ratio $B_2H_6 : NH_3$	Yield of borazole (%)
1	190	3 days	1 : 9	—
1	400	2 hr	1 : 9	—
1	150	2—3 hr	1 : 2	17
1	180	15 min	1 : 2	32
1	180—190	2—3 hr	1 : 2	33
1	200—220	45 min	1 : 2	41
5	200	20 min	1 : 2	23

It is seen from the table that an increase in pressure to 5 atm has an adverse influence on the formation of borazole, because the yield of $B_3N_3H_6$ decreases from 41 to 23 per cent as a result of the formation of a solid residue.

The reaction in this case may be represented by the equation

$$3B_2H_6 + 6NH_3 \xrightarrow[20\ \text{min}]{200°\ 5\ \text{atm}} 0{\cdot}36B_3N_3H_6 + 13{\cdot}8H_2 + 5{\cdot}98BNH_{1{\cdot}27}$$

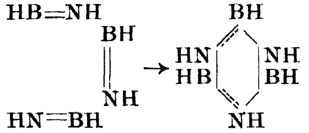
As already mentioned, borazole may be obtained directly from borane and ammonia, but with excess of ammonia above the quantity necessary for the formation of an ammoniate, instead of borazole the main products are borimide and boron nitride according to the reaction

$$B_2H_6 + 6NH_3 \rightarrow 2B(NH_2)_3 + 6H_2$$
$$B(NH_2)_3 \rightarrow BN + 2NH_3$$

With a ninefold excess of ammonia and a temperature of 190°, 80 per cent of diborane is converted into borimide and about 9 per cent into boron nitride. At 400° the yield of boron nitride reaches 35 per cent.

The following mechanism for the formation of borazole from diborane and ammonia is suggested [69]:

$$B_2H_6 \,.\, 2NH_3 \rightarrow 2H_3\overset{-}{B} : \overset{+}{N}H_3 \quad \text{“inorganic ethane”}$$
$$H_3\overset{-}{B}: \overset{+}{N}H_3 \rightarrow H_2B{—}NH_2 + H_2 \quad \text{“inorganic ethylene”}$$
$$H_2B{—}NH_2 \rightarrow HB{=}NH + H_2 \quad \text{“inorganic acetylene”}$$



Borazole—“inorganic benzene”

In the first stage, under the influence of heat, dissociation of the diammoniate into borine ammonia, a compound reminiscent of ethane in structure, occurs. In the second stage the dehydrogenation of borine ammonia with the formation of a compound reminiscent of ethylene takes place. In the third stage this compound dehydrogenates into “inorganic acetylene.” Like acetylene, which forms benzene on heating, the latter intermediate product trimerizes and gives borazole, “inorganic benzene.”

Although the intermediate product, borine ammonia, $H_3B : \overset{+}{N}H_3$, is not isolated, a compound borine trimethylamine $H_3\overset{-}{B} : \overset{+}{N}(CH_3)_3$ similar to it is obtained from diborine and trimethylamine. The abundant formation of hydrogen in the reaction indicates the dehydrogenation of the intermediate products, and this supports the proposed mechanism of the reaction.

Recently a new method of preparation of borazole from lithium borohydride and ammonium chloride was suggested [70]:

$$3LiBH_4 + 3NH_4Cl \rightarrow B_3N_3H_6 + 3LiCl + 9H_2$$

In this case a preliminary synthesis of the boranes is not required. The reaction is carried out by heating the mixture of reagents $LiBH_4$ and NH_4Cl in powder form at a temperature of about 300°.

The mechanism of this reaction is represented in the following way. Ammonium chloride dissociates on heating into ammonia and hydrogen chloride:

$$6NH_4Cl \rightarrow 6NH_3 + 6HCl$$

Hydrogen chloride liberates diborane from the borohydride according to the reaction:

$$LiBH_4 + 6HCl \rightarrow B_2H_6 + 6LiCl + 6H_2$$

The diborane with ammonia gives borazole:

$$3B_2H_6 + 6NH_3 \rightarrow 2B_3N_3H_6 + 12H_2$$

The borohydrides of metals have recently been manufactured on an industrial scale, and therefore borazole can be synthesized in considerable quantities starting from $LiBH_4$ and NH_4Cl. The expediency of replacing $LiBH_4$ by the borohydride of any other more available metal is obvious.

In the development of this method of preparing $B_3N_3H_6$ the influence of temperature, proportion of reagents, time of reaction and pressure on the yield of borazole was studied (Table 40).

Table 40. *Effect of reaction conditions on yield of borazole* [70]

Quantity (moles)		Temperature (°C)	Time of reaction (min)	Yield of borazole (%)
$LiBH_4$	NH_4Cl			
0·243	0·485	285	30	25·7
0·188	0·374	275	30	32·1
0·80	0·11	300	20	35·0
0·46	0·47	300	20	25·0

The yield of borazole is decreased as a result of side reactions. Thus, NH_4Cl reacts with $B_3N_3H_6$ with the formation of halogen derivatives of borazole.

In its theoretical and practical aspects the chemistry of boranes is a new and interesting field of inorganic chemistry. It is closely connected with organic chemistry, because boranes readily give different organic substances containing boron. At the same time, boranes are an interesting field in the general chemistry of boron, which is attracting the increasing attention of investigators [88].

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CHAPTER V

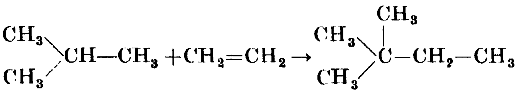
COMPOUNDS OF BORON FLUORIDE IN ALKYLATION REACTIONS

1. ALKYLATION OF ISOPARAFFINS WITH OLEFINES

THE alkylation reaction occupies a special position in the present day organic synthetic industry. It lies at the basis of the production of high octane components, for example, *iso*octane. Important starting materials of synthetic rubbers, plastics, emulsifying agents, etc., are obtained by alkylation [1, 2, 3].

The alkylation of isoparaffins by olefines may be carried out by thermal (high temperature) and catalytic means. Thermal alkylation, in spite of a number of advantages, has not received wide industrial application because, in the presence of special catalysts, the need for the complicated apparatus which is necessary for thermal alkylation at high temperatures and under pressure disappears.

In 1932 V. N. Ipatiev [4] first carried out the catalytic alkylation of isoparaffins with olefines in the presence of $AlCl_3$. This may be considered as an addition reaction of isoparaffins to olefines and for *iso*butane and ethylene on thermal alkylation may be represented by the following scheme:



$$(CH_3)_2CH{-}CH_3 + CH_2{=}CH_2 \rightarrow (CH_3)_2C(CH_3){-}CH_2{-}CH_3$$

With the help of aluminium chloride it is possible to alkylate all paraffins of normal and iso-structure, except methane and ethane, by means of olefines [5]. But the reaction is accompanied by side reactions — polymerization and destructive alkylation — as a result of which the alkylate is a complex mixture of hydrocarbons with a lower octane number than in the product of alkylation with acids. In addition $AlCl_3$ as is known is a very hygroscopic substance and requires special conditions in storage and use ; it often enters into chemical reactions with basic reagents, changes its nature and loses its catalytic activity. As a result of this, processes of alkylation of paraffins with olefines in the presence of $AlCl_3$ have not received wide application in industry. During the second world war 2,3-dimethylbutane was obtained on an industrial scale by the alkylation of *iso*butane with ethylene in the presence of $AlCl_3$ [6].

Other metal halides proposed as catalysts for alkylation, for example $AlBr_3$, have found no application.

The first industrial alkylation process was the sulphuric acid alkylation of isoparaffins with olefines, developed in 1938 [7]. Owing to its simplicity, the cheapness of the catalyst, the wide variety of raw materials and high quality alkylate, this process is at the present time the chief one in industry.

In the presence of 96—97 per cent H_2SO_4 *iso*butane, *iso*pentane and *iso*hexane are comparatively easily alkylated by all olefines, except ethylene, with the formation of an alkylate having a high octane number. *iso*Butane is alkylated with ethylene in the presence of sulphuric acid and salts of silver and mercury which act as promoters.

Alkylation with sulphuric acid, as with $AlCl_3$, is accompanied by isomerization, cracking [8], hydro- and dehydro-polymerization [9], and therefore in the alkylate there are isoparaffins not only of the same structure and molecular weight, which should be expected, arising from the initial isoparaffins and olefines, but also hydrocarbons of smaller and of greater molecular weight [10, 11].

The basic raw material of the sulphuric acid alkylation is the butane—butylene fraction. The most satisfactory conditions are as follows: temperature 0—10°, concentration of sulphuric acid 96—97 per cent, 5—6 times excess of isoparaffin. The total consumption of sulphuric acid is about 200 kg/1000 kg of alkylate obtained [12].

In the U.S.S.R. the sulphuric acid alkylation of *iso*butane and benzene by olefines in industrial conditions was studied in detail by Iu. G. Mamedaliev [11].

During the second world war hydrogen fluoride was vigorously introduced as a catalyst for alkylation [2, 12, 13]. It is characteristic of the alkylation of isoparaffins with olefines in the presence of anhydrous liquid HF that with this catalyst isoparaffins are alkylated not only by butylenes and amylenes, but also with propylene. In the presence of HF the reaction proceeds at room temperature, and, unlike the reaction with H_2SO_4 as a catalyst, is not accompanied by side reactions even with a small increase of temperature. Hydrogen fluoride is used in very large quantities but it can be regenerated. Its total losses in the reaction amount to about 0·2 per cent. Anhydrous HF does not act on steel, and containers made from mild, carbon-free steel are quite suitable for its transport and storage. However, the high volatility of hydrogen fluoride and its high toxicity make difficult its wide use as a catalyst.

The defects of catalysts in general use stimulated the search for new and more effective catalysts.

The first researches on the use of boron fluoride for the alkylation of isoparaffins with olefines date from 1935 [14], i. e. from the period when boron fluoride was still only beginning to be introduced as a catalyst into organic chemistry. After this, investigators occupied with the synthesis of high octane components forgot about it, and only in 1942—1943 did boron fluoride again attract the attention of chemists.

In the presence of BF_3 isoparaffins having a tertiary carbon atom in the molecule are readily alkylated by olefines. The reaction can be carried out at a temperature of 200° or higher. Good results are obtained when the alkylation is carried out in a rotating autoclave at a temperature of 10—30° and a pressure of 5—20 atm in the presence of BF_3 with finely crushed nickel and a small amount of water [14]. In examples of the alkylation of *iso*butane with ethylene and *iso*butylene, and of *iso*pentane with ethylene, it was found that one mole BF_3 can bring about the alkylation of 75 moles of olefine. The results of experiments on the alkylation of *iso*butane with ethylene are given in Table 41.

Table 41. *Alkylation of* iso*butane with ethylene* [14]

Conditions of reaction	Experiment					
	1	2	3	4	5	6
*iso*Butane (g):						
introduced into reaction	160	90	90	90	90	220
reacted	24	88	88	89	88	180
Ethylene (g):						
introduced into reaction	81	130	115	110	90	104
reacted	61	130	115	109	85	104
Catalyst (g):						
BF_3	2	8	8	14	14	30
Ni (powder)	5	5	5	10	10	5
H_2O	0·5	2	2	4	4	25HF
Time of reaction (hr)	32	28	26	21	22	40
Temperature (°C)	20—25	20—30	20—30	20—25	20—25	20—25
Molar ratio of ethylene to *iso*butylene	5·9 : 1	3·1 : 1	2·7 : 1	2·5 : 1	2 : 1	1·2 : 1
n_D^{20} of alkylate (average)	1·4188	1·4126	1·4064	1·3998	1·3984	1·3819
Amount of alkylate boiling up to 225° (%)	37	60	82	85	>90	97

Hydrated boron fluoride of the composition $BF_3 . nH_2O$ ($n = 1—2$), recommended in many patents [15—27] as a catalyst in the alkylation of isoparaffins (*iso*butane, *iso*pentanes) by individual olefines (ethylene) or mixtures of them (ethylene—propylene, ethylene—butylene), possesses high catalytic activity. The catalyst is usually obtained by passing boron fluoride into water until the specific gravity of the saturated solution reaches 1·77, which corresponds to the composition : 79 per cent BF_3 and 21 per cent H_2O [21]. The alkylation is carried out in the liquid phase at temperatures of 30—80° and at increased pressure.

To increase the catalytic activity of boron fluoride, it is used together with mineral acids, in particular with sulphuric [28, 29], fluorosulphonic [30, 31] and especially frequently with hydrofluoric [32—45] and phosphoric acids. When paraffins are alkylated with olefines and BF_3 and HF are used, the former often serves as a promoter. The alkylation of *iso*butane with ethylene is carried out in the following way ; 100 parts by weight of HF, 10 parts by weight of BF_3 and 100 parts by weight of *iso*butane are put into an autoclave. Ethylene is passed into the well stirred mixture at 20° until the pressure reaches 30 atm. After this the introduction of ethylene is stopped, but the vigorous stirring of the mixture is continued for 12 hr. As a result the alkylate is obtained in a yield of 200 parts by weight. Ninety per cent of the alkylate boils up to 205° and 55 per cent (by volume) consists of *iso*hexanes [42].

In the presence of BF_3 and HF normal paraffins are also alkylated by olefines, but at a higher temperature, which is conducive to the isomerization of normal paraffins, and at increased pressure, which guarantees the preservation of the reaction mixture in a liquid condition [43]. To create milder conditions for the reaction and consequently to obtain the primary alkylation products; it is recommended that small amounts (about 10 per cent by weight) of aromatic or naphthenic hydrocarbons be introduced into the reaction mixture [44].

According to certain patents [46], normal paraffins are alkylated by olefines in the presence of free BF_3, but the process is carried out in such a way that first the normal paraffins undergo isomerization in the presence of boron fluoride, and are then alkylated by the olefines with the same catalyst in another zone.

Low-boiling benzines with high octane number are obtained by passing a mixture of gaseous normal paraffins and isoparaffin hydrocarbons with normal gaseous olefines in the presence of BF_3 and HF over finely powdered nickel [47, 48].

In recent years in a series of patents [49, 50] hydrated boron fluoride together with hydrogen fluoride, i.e. the complex $BF_3 . H_2O . HF$, is suggested as a catalyst for the alkylation of isoparaffins with olefines.

The catalytic action of this complex has been studied in the laboratory and in a continuously acting experimental plant for the alkylation of *iso*butane by ethylene to di-*iso*propyl [51]. It was found that when *iso*butane is alkylated with ethylene in the presence of the catalyst $BF_3 . H_2O . HF$ at a temperature of 100—135° and a pressure not greater than 14—17·5 atm an alkylate is obtained with an octane number about 90, containing from 50 to 70 per cent by volume of di-*iso*propyl (2,3-dimethylbutane).

The complex $BF_3 . H_2O . HF$ when continuously activated by boron fluoride retains its catalytic action for a long time and can give, for 1 vol., up to 88 vols. of alkylate, but when the catalyst is activated with anhydrous hydrogen fluoride the increase in its output rises to 195 vols. (for 1 vol. of catalyst). This complex is obtained by passing gaseous BF_3 from a copper cylinder into aqueous hydrogen fluoride in the coppered reaction vessel for the alkylation, and stirring until there is no further increase in weight. The quantity of BF_3 thus absorbed always corresponds to one mole of it to 1 mole of water present in the solution, and does not depend on the concentration of hydrogen fluoride and the pressure, as seen from Table 42.

Table 42. BF_3 *content of the catalyst* $BF_3 . H_2O . HF$

System	Molar ratio BF_3/H_2O	Pressure
$H_2O + BF_3$	0·980	Atmospheric
30% solution $HF + BF_3$	1·018	Atmospheric
40% solution $HF + BF_3$	0·965	Atmospheric
50% solution $HF + BF_3$	1·001	Atmospheric
50% solution $HF + BF_3$	1·010	3·5 atm
60% solution $HF + BF_3$	0·940	Atmospheric

Table 43. *Alkylation of* iso*butane with ethylene in the presence of the catalyst* $BF_3 . H_2O . HF$ *with varying* HF *content*

Conditions of reaction	Catalyst		
	$BF_3 . H_2O$	25% solution of HF saturated with BF_3	50% solution of HF saturated with BF_3
Molar ratio of *iso*-C_4H_{10} : C_2H_4	2·60	2·75	2·84
Taken into reaction:			
*iso*butane (kg)	7·63	7·08	13·93
ethylene (kg)	1·43	1·23	2·37
catalyst (ml)	200	250	250
Time of contact (min)	35	18	19
Temperature (°C)	57	58	56
Pressure (atm)	16	15·7	15·7
Alkylate obtained (kg)	2·47	2·69	6·09
Yield of alkylate (as % of ethylene)	173	219	258
	30% solution of HF saturated with BF_3	40% solution of HF saturated with BF_3	60% solution of HF saturated with BF_3
Alkylate obtained (l.)	100	117	53
Vol. of alkylate for 1 vol. of catalyst	134	195	84

The complex obtained by saturating a 40—50 per cent solution of hydrogen fluoride with boron fluoride is a transparent, white liquid of sp.gr. 1·75, almost inactive on glass and not exerting a specially corrosive action if it falls on the skin, but strongly corroding the ordinary kinds of steel. Copper and brass are quite resistant to the action of the complex and are used for the manufacture of apparatus.

The activity of the catalyst is highest when the ratio $BF_3 : H_2O : HF = 1 : 1 : 1$. But since boron fluoride hydrate itself activates the alkylation of *iso*butane with ethylene, the addition to it of any amounts of HF increases the yield of alkylate, as seen from Table 43.

The dependence of the quality and yield of alkylate on the ratio of the reagents and the temperature is given in Table 44.

Table 44. Alkylation of iso*butane with ethylene in the presence of the catalyst* $BF_3 . H_2O . HF$ *in different conditions*

Conditions of reaction	Experiment			
	1	2	3	4
Molar ratio of *iso*-C_4H_{10} : C_2H_4	2·84	2·84	4·15	4·15
Taken into reaction:				
*iso*butane (kg)	13·93	13·44	14·28	13·86
ethylene (kg)	2·37	2·27	1·72	1·61
catalyst (ml)	200	200	200	200
Temperature (average) (°C)	56	43	56	43
Pressure (atm)	15·7	15·4	13	13
Time of contact (min)	19	18	22	22·5
Total yield of alkylate (kg)	6·09	5·66	3·61	3·62
Conversion of ethylene (%)	95·7	93·3	87·0	86·5
Yield of alkylate (as % of ethylene)	258	249	210	225
Fluorine content of alkylate (wt. %)	0·0026	—	0·0029	0·0038
Octane number of alkylate without TEL	89·0	90·4	88·8	90·3
Octane number of alkylate with 4 ml TEL	107·6	109·0	106·8	108·0
Composition of alkylate (vol. %)				
pentanes	5·2	3·5	4·0	4·0
hexanes	66·6	67·0	70·0	71·0
heptanes	7·8	8·0	6·0	7·5
octanes	13·0	14·5	13·0	11·5
Nonanes and higher hydrocarbons	7·4	7·0	7·0	6·0
Amount of di-*iso*propyl fraction of b. p. 135—140° in alkylate (vol. %)	62·5	63·5	66·0	67·5
Octane number of di-*iso*propyl fraction	91·8	92·5	90·5	91·9
Fluorine content of di-*iso*propyl fraction	0·0030	0·0027	0·0032	0·0037

In work on the experimental plant about 200 kg *iso*butane and 38 kg ethylene were loaded into the system for one cycle and about 80 kg alkylate were obtained.

On account of the experimental results given above, the catalyst $BF_3 . H_2O . HF$ may be considered very effective.

The development of methods of regenerating absorbed BF_3 from hydrocarbons in which it is removed from the alkylate would appear to be an important factor contributing to the rapid introduction of catalysts based on boron fluoride into industrial processes.

Compounds of boron fluoride with phosphoric acids also deserve attention as catalysts for the alkylation of isoparaffins with olefines.

The chemical nature of these compounds was first studied by A. V. Topchiev and Ya. M. Paushkin [12, 52—54].

The alkylation of isoparaffins with olefines in the presence of orthophosphoric acid saturated with boron fluoride [55—57] proceeds in comparatively mild conditions and is not accompanied by side reactions.

A. V. Topchiev and Ya. M. Paushkin studied the alkylation of different isoparaffins with ethylene, propylene and *iso*butylene in the presence of a catalyst of boron fluoride with water, acids and other organic compounds containing oxygen, and came to the conclusion that in all cases boron fluoride forms coordination compounds, and not solutions or simple mixtures, with the substances added to activate it. These coordination compounds may be considered as quite individual independent catalysts possessing different catalytic activity.

*iso*Butane is alkylated by propylene in the presence of BF_3 and H_3PO_4 in the following way [54, 58]. In glass ampoules cooled in liquid oxygen,

Table 45. *Activity of different catalysts in the alkylation of* iso*butane with propylene* [54]

Catalyst	Yield of alkylate (as % of propylene)	d_4^{20} of alkylate	Vol. % of alkylate boiling up to 150°	Time of action of catalyst
$BF_3 . H_3PO_4$	160—180	0·7440	30	Used 10 times without decrease in activity
$H_4P_2O_7 . 2\ BF_3$	160—180	0·709	80	Used 6 times without decrease in activity
$BF_3 . H_2O$	163	0·7240	45	Used 5 times without decrease in activity
$BF_3 . 2\frac{1}{2} H_2SO_4$	155	0·6802	80	Used once
$BF_3 . CH_3COOH$	70	0·6901	—	—
H_2SO_4	40	0·7415	40	Used once
BF_3*	Traces	—	—	—
$BF_3 . NC_5H_5$*	Traces	—	—	—
$BF_3 . O(C_2H_5)_2$*	0	—	—	—
$BF_3 . CH_3COOC_2H_5$*	0	—	—	—

*Literature reference [15].

20—22 g (10 l.) of a mixture of propylene and *iso*butane in a ratio of 1 : 3 or 1 : 2 were liquefied and 5 ml of the catalyst $BF_3 . H_3PO_4$, obtained by passing BF_3 through 100 per cent H_3PO_4 to full saturation, was added. The ampoules were sealed up, placed in a shaker and shaken for a definite time at a temperature of 15—20°, and then cooled and opened. The unreacted hydrocarbons were collected in a gasometer. The same reaction was studied in the presence of sulphuric acid and other coordination compounds of boron fluoride in comparable conditions (10 l. of a hydrocarbon mixture consisting of 2·5 l. propylene and 7·5 l. *iso*butane, at a temperature of 15—20°). The main results are given in Table 45 [5].

The useful life of the catalyst $BF_3 . H_3PO_4$ in the alkylation of *iso*butane with propylene and the influence of the quantities of it on the yield of alkylate are given in Tables 46 and 47 [58].

Table 46. *Useful life of the catalyst* $BF_3 . H_3PO_4$ *in the alkylation reaction* [58]

Number of experiments in which catalyst was used	Yield of alkylate (ml)	Yield of alkylate (as % of propylene)
1	9·0	163
2	9·2	168
4	8·5	155
6	8·9	160

Table 47. *Influence ot the amount of catalyst* $BF_3 . H_3PO_4$ *on the yield of alkylate* [58]

Amount of catalyst ml/10 l. gas ($iso\text{-}C_4H_{10}$—C_3H_6)	Yield of alkylate (ml)	Yield of alkylate (as % of propylene)
1·0	1·1	20
2·5	4·2	76
5·0	9·0	163
10·0	8·5	155

From the results given it is seen that in the alkylation of *iso*butane with propylene the most active catalyst is the coordination compound $BF_3 . H_3PO_4$. This catalyst does not lose its activity after repeated use, enables a high yield of alkylate boiling mainly within the limits 40—225° to be obtained, does not dissolve in the alkylate and is used up only on account of mechanical losses. When the quantity of $BF_3 . H_3PO_4$ is increased to 5 ml/10 l. of *iso*butane–propylene mixture the yield of alkylate increases. Increasing the amount of $BF_3 . H_3PO_4$ above 5 ml does not increase the yield of alkylate.

In Table 48 some general characteristics of the efficiency of the catalyst $BF_3 . H_3PO_4$ in the alkylation of *iso*butane and *iso*pentane with different olefines are given [54].

Table 48. Alkylation of isoparaffins by olefines in the presence of $BF_3 . H_3PO_4$ [54]

Reagents		d_4^{20} of alkylate	Yield of alkylate as (% of olefine)	Alkylate boiling up to 150° (vol. %)
isoparaffins	olefines			
iso-C_4H_{10}	C_2H_4	0·649—0·664	170	85
iso-C_4H_{10}	C_3H_6	0·744	180	39
iso-C_4H_{10}	*iso*-C_4H_8	0·715	130	60
iso-C_5H_{12}	C_2H_4	—	150	77
iso-C_5H_{12}	C_3H_6	0·705	185	83

In the presence of BF_3 or its coordination compounds with ethyl ether and ethyl acetate, the alkylation of *iso*butane with ethylene scarcely occurs. Sulphuric acid saturated with boron fluoride is an active catalyst for alkylation, but when this catalyst is used repeatedly it loses its activity. Good results are obtained in the presence of boron fluoride hydrate at 20—30°. However, it also is much less effective than $BF_3 . H_3PO_4$ in its activity, and chiefly in its useful life. The fractional composition of the alkylate is given in Table 49.

Table 49. Fractional composition of alkylate obtained in the alkylation of iso*butane with propylene**

Boiling range (°C)	Amount of fraction (vol. %)	d_4^{20} of fraction
40—100	14	0·6831
101—125	8	0·7020
126—150	17	0·7308
151—175	6	0·7560
176—200	15	—
201—225	19	—
Over 226	21	—

*It should be observed that an alkylate of this composition is obtained with insufficient stirring; 85—90 per cent of the alkylate obtained in the conditions of the experiment boils up to 170°.

The activity of different catalysts based on BF_3 in the alkylation of *iso*pentane with ethylene [10, 59] and propylene [60] proved to be the approxymately same, as is evident from Tables 50 and 51.

In the alkylation of *iso*pentane with ethylene in the presence of $H_4P_2O_8.2\,BF_3$ and $H_3PO_4 . BF_3$, for each experiment 50 ml *iso*pentane, 4·5 l. ethylene and 20 ml catalyst were taken. The ethylene was passed through at a rate of 1·5 l./hr; the ethylene which did not enter into the reaction was collected in a gasometer. In eight experiments conducted successively with $H_4P_2O_7 . 2\,BF_3$ the activity of the catalyst was not reduced.

Table 50. *Alkylation of* iso*pentane by ethylene*

Catalyst	d_4^{20} of alkylate	Yield of alkylate as % of ethylene taken for reaction
$H_4P_2O_7 . 2\,BF_3$	0·688	181
	0·690	178
$BF_3 . H_3PO_4$	0·689	183
	0·690	182
$BF_3 . H_2O$	0·692	171
	0·6881	200
	0·683	190

Table 51. *Alkylation of* iso*pentane by propylene*

Catalyst*	Yield of hydrocarbons boiling above 50°		d_4^{20} of alkylate	Useful life of catalyst
	(% of theory)	(% of propylene)		
$BF_3 . H_3PO_4$	73·6	175	0·743	May be used repeatedly
$H_4P_2O_7 . 2\,BF_3$	71·5	170	0·710	
$BF_3 . H_2O$	70·5	168	0·707	
$BF_3 . 2\frac{1}{2}H_2SO_4$	69·0	164	0·705	Activity reduced after first experiment
$BF_3 . CH_3OH$	43·0	105	0·753	
$BF_3 . C_2H_5OH$	33·0	90	0·771	
$BF_3 . HPO_3$	23·0	55	0·730	Practically inactive
$BF_3 . CH_3COOH$	19·0	45	0·690	
$BF_3 . NC_5H_5$	0	0	—	
$AlCl_3$	40	95	0·759	Activity quickly falls
H_2SO_4 (101%)	70	165	0·707	May be used once

*The catalysts $BF_3 . O(C_2H_5)_2$, $BF_3 . CH_3COOC_2H_5$, $BF_3 . PO(OC_6H_4CH_3)_3$ and BF_3 proved to be inactive.

For the alkylation of *iso*pentane with propylene, 50 ml *iso*pentane, 14·5 ml propylene and 20 ml catalyst were placed in a reaction vessel. The reaction was carried out at a temperature of 15—20° and with stirring at a rate of 1500—1600 rev/min. The apparatus shown in Fig. 17 was used for the alkylation.

In Table 52 the fractional composition of the alkylate obtained by the alkylation of *iso*pentane with ethylene in the presence of $BF_3 . H_2O$ is given [12]. By studying the composition of the fractions of alkylate by the method of Raman spectra, it was found that they were mixtures of paraffins and did not contain hydrocarbons of other classes.

Table 52. Chemical composition of some fractions of products of alkylation, with the catalysts $BF_3 . H_2O$ *and* $H_3PO_4 . BF_3$ [12]

Components of reaction	Heptane fraction b. p. 80—90°		Octane fraction b. p. 100—120°	
	Hydrocarbons	Composition (%)	Hydrocarbons	Composition (%)
iso-C_5H_{12} + C_2H_4	2,3-Dimethylpentane	48	2,2-Dimethylhexane	70
	2,4-Dimethylpentane	37	2,5-Dimethylhexane	30
iso-C_4H_{10} + C_3H_6*	2,3-Dimethylpentane	69	2,2,4-Trimethylpentane and others	—
	2,4-Dimethylpentane	29		
iso-C_4H_{10} + C_4H_8*	—	—	2,2,4-Trimethylpentane	50

*An alkylate obtained in the experimental conditions at about 185° with a yield of 180—240% of the olefines and with a sp. gr. 0·700 (at 20°).

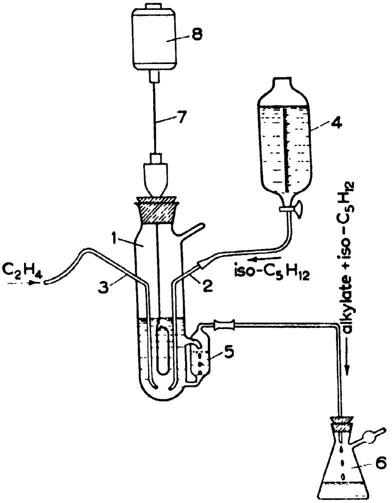


Fig. 17. Continuous action apparatus for the alkylation of *iso*pentane by olefines. 1 — reaction vessel; 2 — tube for introducing *iso*-C_5H_{12}; 3 — tube for introducing C_2H_4; 4 — graduated container for *iso*pentane; 5 — separator; 6 — receiver; 7 — stirrer; 8 — motor.

$\overleftarrow{iso\text{—}C_5H_{12}}$ $\downarrow$ alkylate + *iso*-C_5H_{12}

The alkylate consists of a light part boiling up to 170—180° and a heavy residue. Judging from the bromine value and other physicochemical constants the heavy residue of alkylate also consists of a mixture of isoparaffins, while when the alkylation takes place in the presence of sulphuric acid the bromine value of the heavy fractions of alkylate is equal to 10—15 as a result of the accumulation of olefines in them [12].

A study of the reaction of *iso*pentane with *iso*butylene in the presence of certain coordination compounds of boron fluoride showed that alkylation takes place with the catalyst $BF_3 . H_2O$, but in the presence of coordination compounds of boron fluoride with ethyl ether and pyridine the polymerization of the olefine takes place [12].

According to certain patents [61], isoparaffins are easily alkylated by olefines at a temperature of 0—50° in the presence of boron fluoride together with mono- and difluorometaphosphoric acids.

Waste extract oils are alkylated by olefines with the catalyst $BF_3 . H_2O$ [62].

In this way it is probably possible to confirm that isoparaffins are comparatively easily alkylated by olefines in the presence of coordination compounds of boron fluoride with all substances containing hydroxyl groups, or with HF. Etherates of boron fluoride and also coordination compounds of it with amines are catalytically inactive.

Boron fluoride together with alkyl fluorides is also recommended as a catalyst for alkylation. When boron fluoride, for example, is passed for 45—60 min into a mixture of *iso*butane, ethylene and *iso*propyl fluoride, di*iso*propyl is obtained in 25 per cent yield [63]. The alkylation of *iso*butane with propylene and *iso*butylene is carried out in a similar way. In the presence of this catalyst *iso*butylene may undergo auto-alkylation, the principal direction of which may be represented by the following scheme [64]:

$$BF_3 + 2\,(CH_3)_2CHF + 4\,(CH_3)_2CHCH_3 \rightarrow 2\,(CH_3)_2CHCH_2C(CH_3)_3 + 2\,C_3H_8 + BF_3 . 2HF$$

Diolefines in the presence of boron fluoride do not alkylate isoparaffins, but polymerize [65—67].

The alkylation of isoparaffins by olefines is a very complex process, depending on many factors. For the most part the alkylation is not stopped on the formation of the primary products but is accompanied by a subsequent further alkylation of the isoparaffins formed and by other side reactions, as a result of which a complex mixture of isoparaffins is obtained.

It appears that the complex compounds $BF_3 . H_3PO_4$ and $BF_3 . H_2O . HF$ should be considered the most effective catalysts for the alkylation of isoparaffins with olefines. These catalysts are devoid of many imperfections characteristic of H_2SO_4 and HF; they are convenient to use,* do not require complicated apparatus and precautions necessary, for example, when HF is used, and they enable the alkylate to be obtained in high yields and approximating in quality to the products of the primary reactions. But above all, these two catalysts may be used repeatedly without losing their activity, and consequently may be used in minimum quantities. It seems to us that there are no reasons why the specified catalysts should not be used in industrial processes in the near future.

2. ALKYLATION OF NAPHTHENE HYDROCARBONS WITH OLEFINES

Naphthenes are alkylated by olefines in the presence of BF_3 and its coordinated compounds with water [68] or hydrogen fluoride [69, 70] at a temperature of 20—75° and atmospheric or increased pressure with the formation of alkylnaphthenes according to the reaction

$$\underset{\text{naphthene}}{C_mH_{2m}} + \underset{\text{olefine}}{C_nH_{2n}} \rightarrow \underset{\text{alkylnaphthene}}{C_mH_{2m-1}C_nH_{2n+1}}$$

In contrast to the catalyst $AlCl_3$ which alkylates all naphthenes, boron fluoride possesses great selectivity of action and does not activate, for example, the alkylation by ethylene of *cyclo*hexane, as of normal paraffins. Naphthenes containing tertiary carbon atoms in the ring (methyl*cyclo*pentane and methyl*cyclo*hexane) are comparatively easily alkylated by ethylene in the presence of BF_3. If 60 g methyl*cyclo*pentane react for 20 hr with 50 g ethylene in the presence of 15 g BF_3, 2 g H_2O and 5 g Ni (powder) at a temperature of 20—30°, alkylnaphthenes are obtained in a yield of 33 per cent of the theoretical calculated on naphthene [68]. The reaction is accompanied by partial polymerization of the olefines, and by cleavage and enlargement of the naphthene ring. Therefore, when alkyl*cyclo*pentanes are alkylated with propylene in the presence of BF_3 and HF in suitable conditions, alkylated derivatives of *cyclo*hexane are obtained as the main product [70].

3. ALKYLATION OF AROMATIC HYDROCARBONS WITH OLEFINES AND THEIR DERIVATIVES

Many alkylbenzenes are valuable components of aviation spirit. They are stable, have a high octane number, good lead susceptibility, have a high calorific value, and from this point of view are valued higher than isoparaffins. In recent years the production of cumene has been evolved at a particularly rapid rate, because benzine, which contains this component, is suitable for aeroplane engines with high degrees of supercharge. Many thousands of tons of ethyl benzene and *iso*propyl benzene are produced as starting material for the manufacture of styrene and methyl styrene, which are used in the production of synthetic rubbers and resins. Dodecyl benzene and alkyl naphthalenes, the sulphonates of which were used as detergents and emulsifiers in emulsion polymerization, are attracting great attention. Thus, the importance of alkyl-substituted aromatic hydrocarbons is very great.

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* However, $BF_3 \cdot H_2O \cdot HF$ corrodes steel to a considerable extent.

Among the different methods for the preparation of alkylbenzenes the most up-to-date and convenient is the catalytic alkylation of aromatic hydrocarbons with olefines, alkyl halides, alcohols, ethers and esters in the presence of the catalysts H_2SO_4, H_3PO_4, HF, $ZnCl_2$, $AlCl_3$, $FeCl_3$, BF_3, etc.

The presence of inexhaustible sources of olefines, the simplicity of the technological process of direct alkylation of benzene and its homologues by olefines and the good yields of the intended products, alkyl benzenes, render the method unrivalled among all the others, and the rapidly growing demand for alkyl benzenes guarantees excellent prospects for it.

The property of benzene of being alkylated by olefines in the presence of $AlCl_3$ was discovered by Balson in 1879 [71]. Throughout the past 75 years this reaction has attracted the attention of many research workers, and at the present time it is used in industry, notwithstanding the serious defects of aluminium chloride as a catalyst.

The first investigations on the use of boron fluoride for the alkylation of aromatic hydrocarbons by olefines were completed in 1935. Since then the alkylation of benzene by many olefines in the presence of BF_3 and its coordination compounds has been widely studied. The reaction of benzene with ethylene and propylene, as a result of which the practically important ethyl benzene and *iso*propylbenzene are obtained, has attracted particular attention. Usually 2 — 10 moles benzene are taken per 1 mole olefine, in order to avoid the formation of large quantities of polyalkyl benzenes.

Benzene can be alkylated with ethylene in the presence of BF_3 at a comparatively low temperature and at atmospheric pressure [72], but the reaction takes place more readily at increased pressure. If 250 ml benzene react with 22 g ethylene in the presence of 18 g BF_3 and 2 g H_2O for 8 hr in a revolving autoclave (nickel plated inside) at a temperature of 20—25° and a pressure of 20 atm at first and 10 atm at the end, mono- and di-ethylbenzene are obtained in yields of 21 and 3 per cent respectively [73]. The accelerating action is attributed to the nickel-plated walls of the autoclave. As Ipatiev [74] showed, 1 vol. of BF_3 at a suitable temp-

and reaction time can convert up to 50 vols. of ethylene into ethyl benzene.

Propylene alkylates benzene more easily than ethylene. This reaction has been studied in detail in the presence of "solutions", or rather coordination compounds, of boron fluoride with a number of organic and inorganic substances [75]. It was found that the degree of alkylation and the composition of the reaction products depended on the rate of flow of propylene into the mixture of benzene and the catalyst, but chiefly on the nature of the substance in which the BF_3 is dissolved. In the presence of boron fluoride dissolved in ethers and esters, alkylation hardly takes place at all. The catalytic action of BF_3 increases in proportion to the increase in acidity of the solvent. When boron fluoride is used in organic acids, benzene is alkylated by propylene more easily the stronger the acid. The most active catalysts are solutions of boron fluoride in concentrated sulphuric acid and in phenol. But the catalyst $BF_3 + H_2SO_4$ loses its activity in the course of time, and therefore the rate of alkylation gradually decreases. The catalyst $BF_3 + C_6H_5OH$ does not lose its catalytic activity in use, and gives a complex mixture of alkylation products up to tetra*iso*propylbenzene. Pure boron fluoride has little activity as a catalyst, although in some patents [76—78] it is recommended as a catalyst for this reaction. The main alkylation products, the di*iso*propylbenzenes, consist of 98 per cent *p*- and 2 per cent *o*-di*iso*propylbenzene.

Table 53. Alkylation of benzene with propylene in the presence of BF_3 *dissolved in different reagents*

Taken for reaction				Propylene absorbed (g)	Time of absorption of propylene (hr)	*iso*Propylbenzenes obtained (g)				
Benzene (ml)	BF_3 (g)	Promoter formula	(g)			mono-	di-	tri-	tetra-	total
1·93	7·4	$CH_3COOC_2H_5$	9·6	0	3·5	traces	0	0	0	0
1·93	8·2	$CH_3CH_2OC_2H_5$	8·8	0	5·0	0	0	0	0	0
1·93	9·0	CH_3COOH	8·0	0	3·5	2	0	0	0	2
1·93	1·5	$CH_2ClCOOH$	16·0	0	3·5	9	0	0	0	9
1·93	1·5	CCl_3COOH	29·0	0	3·5	17	0	0	0	17
1·93	2·4	H_2SO_4	17·0	66	1·0	109	34	0	0	143
1·93	8·5	H_2SO_4	49·5	140	1·5	34	190	0	0	224
1·93	9·7	H_2SO_4	50·3	188	4·0	20	237	traces	0	257
1·93	1·5	$H_2SO_4 + 15\%SO_3$	21·0	77	1·0	76	105	0	0	181
2·30	3·0	C_6H_5OH	17·0	43	1·2	36	8	15	0	59
6·20	4·0	C_6H_5OH	6·0	451	—	173	221	126	88	608

The results of the most characteristic experiments are summarized in Table 53.

Benzene and propylene, heated in a ratio of 2 : 1 for 2 hr at 150° in the presence of a catalyst prepared by heating BF_3 with C_5H_{12}, give mono-, di- and poly*iso*propylbenzene with a yield of 21·5 and 2 per cent respectively [79].

In a number of patents [80—82] boron fluoride hydrates are suggested as effective catalysts for the alkylation of benzene with ethylene, propylene and the higher olefines. Thus, benzene with ethylene and propylene in the presence of $BF_3 . H_2O$, under a pressure sufficient to keep the olefines in the liquid state, form alkylbenzenes with a yield of 82 and 62 per cent respectively [80].

Since 1946 a mixture of boron fluoride and hydrogen fluoride has been used as a catalyst for the alkylation of benzene with olefines. There is no doubt that in this particular case also a coordination compound $BF_3 . HF$ is formed, which acts as the catalyst. This is confirmed by the observation that each one of these substances separately does not activate the alkylation with ethylene, but taken together they are a good catalyst. It is known, for example, that in the presence of hydrogen fluoride only benzene does not react with ethylene. Moreover, this reaction does not go vigorously enough with BF_3 alone. If, however, the reaction between benzene and ethylene (in the ratio of 1 : 0·2) is carried out in the presence of BF_3 and HF at a temperature of 220° and increased pressure, ethyl benzene is obtained in a yield of about 86 per cent of the theoretical [83]. Similarly benzene is alkylated with propylene in the presence of BF_3 and HF or sodium and potassium fluorides [84—86].

Compounds of boron fluoride with phosphoric acids, especially orthophosphoric acid, are highly effective catalysts for the alkylation of benzene with olefines.

For the preparation of the catalyst 70—100 per cent H_3PO_4 is recommended, but preference is given to 100 per cent orthophosphoric acid, because, when 70—90 per cent H_3PO_4 is used, there is probably formed a mixture of the composition $BF_3 . H_3PO_4 + BF_3 . H_2O$ which is less active as a catalyst than the coordination compound $BF_3 . H_3PO_4$.

The catalyst $BF_3 . H_3PO_4$ has a very high activity in the alkylation of aromatic hydrocarbons by olefines, is not poisoned for a long time and is sparingly soluble in hydrocarbons, which enables it to be separated after the reaction and used again. In the presence of this catalyst alkylbenzenes are obtained in high yield even at a temperature of 80—120°, atmospheric pressure and a ratio of benzene to olefine of 1—1·5 : 1, although to guarantee a high yield of monoalkylbenzenes it is recommended that benzene be used in four- or fivefold excess. Benzene (4·5 moles) and ethylene (4 moles) in the presence of $BF_3 . H_3PO_4$ (100 ml), prepared by saturating BF_3 with 85 per cent H_3PO_4 at 85—100° and increased pressure (10·7 atm), form an alkylate with a 70 per cent yield (relative to benzene), which consists of 85 per cent of ethylbenzene and 15 per cent of diethylbenzene [87]. In a similar way benzene is alkylated by other olefines.

A. V. Topchiev and Ya. M. Paushkin studied in detail the alkylation of benzene with ethylene and propylene in the presence of $BF_3 . H_3PO_4$, obtained by saturating 100 per cent H_3PO_4 with boron fluoride [88, 89]. Periodical alkylation was carried out in a three-necked flask, provided with a stirrer with a mercury seal. For propylation 350 ml (308 g) benzene, 30·5 l. (53·4 g) propylene (97—98 per cent unsaturated) and 20 ml of the catalyst $BF_3 . H_3PO_4$ were introduced into the flask. Thus, the weight ratio of the reagents was 5·7 : 1 and the volume ratio of catalyst to benzene 1 : 17·5. At the end of the reaction the hydrocarbon layer was separated from the catalyst, washed, dried and distilled with a column with an efficiency of 12 theoretical plates. *iso*-Propylbenzene was obtained in a yield of 159 per cent of the propylene, and the total yield of alkylate amounted to 196 per cent. One and the same catalyst was used in several experiments. In addition, it was not poisoned and its activity was not reduced on repeated use. In later experiments the yield of $C_6H_5 . C_3H_7$ was increased on account of improved stirring.

Table 54. *Yield of* iso*propylbenzene in the alkylation of benzene with propylene in the presence of different catalysts*
(molecular ratio $C_6H_6 : C_3H_6 = 2 : 1$)

Catalyst	Amount in alkylate before distillation		Yield of *iso*propylbenzene (b. p. 152—153°)		Consumption of catalyst (% of *iso*-propylbenzene)**
	of *iso*propylbenzene	of poly*iso*propylbenzene	(% of theoretical)	(% of propylene)	
$H_3PO_4 . BF_3$	53·0	5·0	91·0	259	<1
$H_3PO_4 . BF_3$*	53·6	4·6	82·0	239	2—3
$AlCl_3$	39·2	14·6	51·0	145	5—6
$AlCl_2 . HSO_4$	32·2	22·0	49·0	—	15
$H_2O . BF_3$	56·8	2·5	82·8	239	—
H_2SO_4	47·6	8·8	62·1	178	23

*The catalyst is prepared from 88·7% H_3PO_4.
**In laboratory experiments.

The composition and yield of the alkylation products with different catalysts are given in Table 54 [88].

To ensure high yields of monoalkylbenzenes A. V. Topchiev and Ya. M. Paushkin [12] used a laboratory apparatus for the continuous alkylation of benzene with olefines (Fig. 18), which enables a large excess of benzene to be held in the reaction vessel, but in equimolecular quantity in relation to the propylene in the whole system [89].

Furthermore, A. V. Topchiev, Ya. M. Paushkin, I. F. Baev and M. V. Kurashov checked the process of alkylation of benzene with propylene on a large scale in an experimental industrial plant, in which a strong preference for the catalyst $H_3PO_4 \cdot BF_3$ over the others used in industry was confirmed.

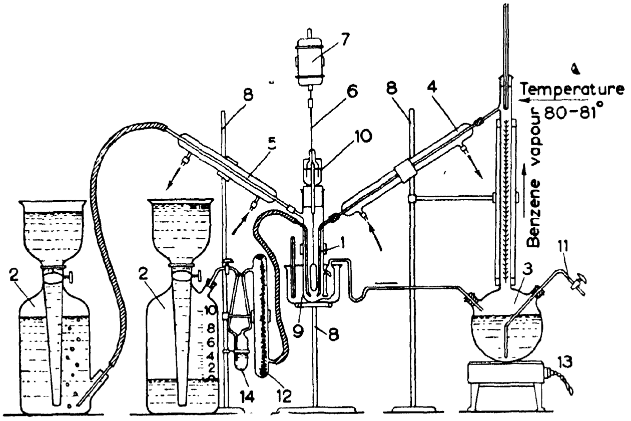


Fig. 18. Continuous action apparatus for the alkylation of benzene by olefines. 1 — reaction vessel; 2 — gasometers; 3 — distillation flask with fractionating column; 4 — direct condenser; 5 — reflux condenser; 6 — stirrer; 7 — motor; 8 — stands; 9 — cooling bath 10 — mercury seal; 11 — syphon for discharge of alkylate; 12 — drying column; 13 — electric hot plate; 14 — bubble counter.

Temperature ← 80–81°

↑ Benzene vapour

Ethylene alkylates benzene at atmospheric pressure less vigorously than propylene.

Benzene and its homologues are also alkylated by higher olefines, for example, di*iso*hexylene or mixtures of hydrocarbons containing considerable amounts of olefines in the presence of the catalyst $H_3PO_4 \cdot BF_3$ [90]. Secondary butylbenzene with a gaseous mixture of saturated hydrocarbons containing 23 per cent by volume of butylenes, with the catalyst $BF_3 \cdot H_3PO_4$ (reaction mixture : catalyst = 4 : 1) forms di-*sec.*-butylbenzene [91].

For the alkylation of benzene with ethylene, propylene and other olefines it is also recommended to use as catalyst boron fluoride together with fluorosulphonic acid [92], organic acids [93], alcohols [94], and as other complexes [95]. The catalyst boron fluoride + alcohol is prepared by saturating an alcohol containing 1—8 atoms of carbon with BF_3 until products of the composition $BF_3 . ROH$ or $BF_3 . 2ROH$ are formed. For the alkylation of benzene with propylene, 440 g (5 · 6 moles) benzene, and 77 g (50 ml) $BF_3 . CH_3OH$ are introduced into the reaction flask provided with a mechanical stirrer and propylene is passed into the vigorously stirred mixture at a rate of 90 ml/min at a temperature of 80—90° and atmospheric pressure. As a result of the reaction 450 g of alkylate, consisting of 62 per cent *iso*propylbenzene and 38 per cent di*iso*propylbenzene, is obtained [94]. Benzene and *cyclo*hexene in the presence of BF_3 with HCl are converted into mono- and di*cyclo*hexylbenzenes [96, 97].

Homologues of benzene are alkylated by olefines more easily than benzene itself. Toluene, ethyl benzene and *iso*propyl benzene are alkylated by propylene even in the presence of boron fluoride etherates, which have a reduced catalytic action in the alkylation of benzene with olefines [98, 99].

Condon [98] studied the relative rate of propylation of benzene, toluene ethyl benzene, *iso*propylbenzene and *tert.* —butylbenzene in the presence of $BF_3 . O(C_2H_5)_2$ in conditions which exclude the possibility of the dialkylation of the *iso*propyl derivatives (time of reaction 2·5—5 hr; temperature 40°) and found the following sequence of change of rate: 1·2, 1·0, 1·8, 1·7 and 1·4 respectively. The author considers it probable that the main reason for the difference in the rate of alkylation of the specified hydrocarbons is the steric hindrance of the reaction in the *o*-positions, which increases as the alkyl group linked to the benzene nucleus becomes larger. Thus, the rate of introduction of the radical into the *m*- and *p*-positions is approximately identical for $C_6H_5CH_3$ and $C_6H_5CH(CH_3)_2$ while the rate of introduction in the *o*-position for $C_6H_5CH(CH_3)_2$ is six times smaller than the rate of introduction of the *iso*propyl radical into the *o*-position of toluene.

However, there also exist results according to which in some conditions benzene is alkylated by propylene twice as easily as, for example, ethyl benzene [75].

This discrepancy may be explained by the capacity of polyalkylbenzenes on the one hand to be dealkylated to less highly alkylated benzenes, and on the other hand to alkylate benzene. In the case of the reaction of ethylbenzene with propylene the ethylpropylbenzenes formed on dealkylation reduce the yield of alkylbenzenes. Then, as also in the alkylation of benzene with propylene, the di*iso*propylbenzenes formed on dealkylation will themselves alkylate benzene and at the same time increase the total yield of mono*iso*propylbenzene.

Toluene and propylene at 65° form a mixture of *o*-, *m*- and *p*-thymols in the proportion 37·6, 27·5 and 34·9 per cent respectively [99]. Benzene and 2,6-dimethylbi*cyclo*(3,2,1)-2-octene are converted into 2-phenyl-2,6-dimethylbi*cyclo*(3,2,1)-octane [100]. *p*-Ethyltoluene and 4-methyl*cyclo*hexene form 1-methyl-4-ethyl-?-(methyl*cyclo*hexyl) benzene and 1-*p*-tolyl-2-(methyl-5-ethyl-phenyl) ethane [101].

Other more complex aromatic hydrocarbons also combine with olefines or *cyclo*olefines in the presence of BF_3 and form corresponding derivatives [102—108]. For example, diphenyl [103], diphenylbenzene [104] and unsymmetrical diphenylethane [105] with *cyclo*hexene in the presence of BF_3 form cyclohexylated derivatives with one or a greater number of *cyclo*hexyl radicals. 1,3-Dimethyl-1,3-diphenyl*cyclo*butane with olefines or *cyclo*olefines in the presence of BF_3 is converted into the corresponding derivatives [106]. The alkylation of halobenzenes by olefines with a BF_3 catalyst has not yet been described.

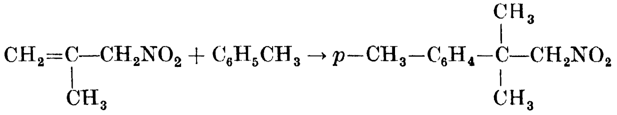
As a conclusion of this paragraph the qualitative characteristics of the activity of different catalysts based on boron fluoride in the alkylation of isoparaffins and benzene with olefines are given in Table 55. The plus sign indicates that the reaction works, the minus sign that the reaction is absent.

Table 55. *Alkylation of isoparaffins and benzene with olefines*

Catalyst	Alkylation of *iso*butane and *iso*pentane				Alkylation of benzene		Remarks
	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_2H_4	C_3H_6 and C_4H_8	
$BF_3 . H_2O$	+	+	+	+	+	+	Active catalyst
$BF_3 . 2\,H_2O$	—	—	—	—	—	—	Hydrocarbons not alkylated
$BF_3 + H_2SO_4$	—	+	+	+	+	+	Active
$BF_3 . H_3PO_4$	+	+	+	+	+	+	Very active catalyst
$H_4P_2O_7 . 2\,BF_3$	+	+	+	+	+	+	Very active catalyst
$BF_3 . H_2O . HF$	+	+	+	+	+	+	Very active catalyst
$HF + BF_3(HBF_4)$	+	+	+	+	+	+	Very active catalyst
$BF_3 . HPO_3$	—	—	+	+	—	+	Not very active cat.
$BF_3 . CH_3OH$	—	—	+	+	—	+	Not very active cat.
$BF_3 . O(C_2H_5)_2$	—	—	—	—	—	+	Not very active cat.
$BF_3 . NR_3$	—	—	—	—	—	—	Does not alkylate
H_2SO_4	—	+ poor	+	+	—	+	Good catalyst
H_3PO_4	—	—	—	—	—	+	—

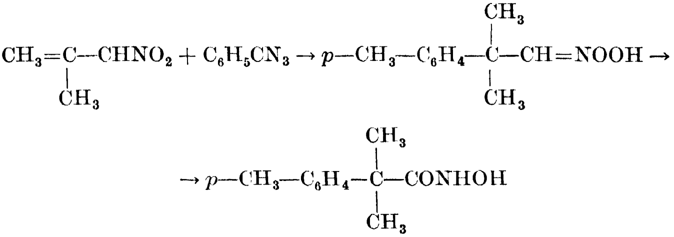
4. ALKYLATION OF AROMATIC HYDROCARBONS WITH SUBSTITUTED OLEFINES

In the presence of BF_3 aromatic hydrocarbons combine with substituted olefines at the double bond. Nitro-olefines add on aromatic hydrocarbons and give the corresponding nitroalkylbenzenes. The course of the reaction depends on the structure of the nitro-olefines . β,γ-Nitro-olefines normally react with toluene in the presence of BF_3; for example, 2-methyl-3-nitropropene gives 2-methyl-2-*p*-tolyl-1-nitropropane [109]:



$$CH_2{=}\underset{CH_3}{C}{-}CH_2NO_2 + C_6H_5CH_3 \rightarrow p{-}CH_3{-}C_6H_4{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2NO_2$$

α,β-Nitro-olefines reacting with toluene in the presence of BF_3 form a complex mixture of products, for example, 2-methyl-1-nitropropene gives a mixture consisting of 2-methyl-2-*p*-tolyl-1-nitropropane, a small quantity of a solid, unidentified substance of the composition $C_{11}H_{13}ON$ and 22 per cent of the theoretical yield of α-(*p*-tolyl)-*iso*butyrohydroxamic acid. The latter is probably formed by 1,4-addition to the nitro-olefine and by subsequent regrouping of the acinitro-compound formed, according to the scheme



$$CH_3{=}\underset{CH_3}{C}{-}CHNO_2 + C_6H_5CN_3 \rightarrow p{-}CH_3{-}C_6H_4{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH{=}NOOH \rightarrow$$

$$\rightarrow p{-}CH_3{-}C_6H_4{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CONHOH$$

In an attempt to alkylate benzene with 2-methyl-1-nitropropene in the presence of BF_3, small quantities of a solid, unidentified product of the composition $C_{10}H_{11}ON$ are obtained. In the presence of $AlCl_3$ this reaction proceeds comparatively easily with the formation of α,β-dichlor*iso*butyraldoxime $(CH_3)_2CCl$-$CCl = NOH$ and α-phenyl*iso*butyrohydroxamyl chloride $C_6H_5C(CH_3)_2CCl = NOH$.

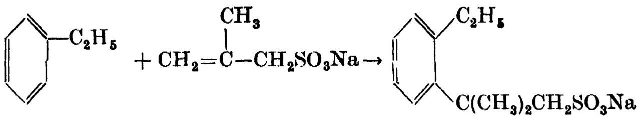
*Preparation of 1-Nitro-2-*p*-tolyl-2-methylpropane [109]*

Ten grammes of 2-methyl-3-nitropropene in 100 ml toluene were saturated with BF_3. The mixture was left overnight at room temperature, and then heated for 1 hr at 70—80°, cooled, washed with water and distilled. Five grammes of the product, a pale yellow oil of b.p. 145—150°/13 mm; $n_D^{22} = 1 \cdot 5258$ was obtained.

*Preparation of α-(*p*-tolyl)-isoButyrohydroxamic Acid*

Twenty grammes of 2-tolyl-1-nitropropene in 100 ml toluene were saturated with BF_3 at 50°. The excess of BF_3 was removed by blowing air through the solution and the latter was washed with water. The yield of α-(*p*-tolyl)-*iso*butyrohydroxamic acid was 8·5 g and after recrystallization from benzene it consisted of colourless, fibrous needles of m.p. 157°. It dissolves in a dilute aqueous solution of NaOH, but does not dissolve in $NaHCO_3$ solution; with $FeCl_3$ it gives a reddish-violet coloration.

Propene- and *iso*butene-sulphonic acids [110] and their sodium salts [111], for example, sodium 2-methyl-2-propenesulphonate, $CH_2 = C(CH_3)CH_2SO_3Na$, with alkylbenzenes in the presence of BF_3 form aryl substituted aliphatic sulphonic acids. This fact is a conclusive proof that the reactions considered above proceed by the addition of aromatic hydrocarbons at the double bond of the olefines. BF_3 is generally used with sulphuric acid. The reaction with ethyl benzene is carried out in the following way: 10 g $CH_2 = C(CH_3)CH_2SO_3Na$, 85 ml $C_6H_5C_2H_5$ and 5 ml 96 per cent H_2SO_4 are treated with BF_3 for 30 min; the mixture is left for 2 hr with continuous stirring. After removal of BF_3 by blowing air through, sodium 2-(2-ethylphenyl)-2-methylpropanesulphonate separates from the reaction mixture:



These sulphonates are readily soluble in water and possess emulsifying properties.

Vinyl compounds also add on aromatic hydrocarbons at the double bond in the presence of BF_3 [112]:

$$\begin{array}{lll} C_6H_6 + CH_2 = CHOC_2H_5 & \rightarrow & C_6H_5CH_2CH_2OC_2H_5 \\ C_6H_6 + CH_2 = CHOOCCH_3 & \rightarrow & C_6H_5CH_2CH_2OOCCH_3 \\ C_6H_6 + CH_2 = CHCOOH & \rightarrow & C_6H_5CH_2CH_2COOH \\ C_{10}H_8 + CH_2 = CHCOCH_3 & \rightarrow & \gamma\text{-hydroxybutylnaphthalene} \end{array}$$

Derivatives of acids of the type Ar . O . RCOOH with polymerized olefines in the presence of BF_3 form compounds alkylated in the aromatic nucleus [113].

5. ALKYLATION OF AROMATIC HYDROCARBONS WITH ACETYLENE AND DIENE COMPOUNDS

Acetylene and diene hydrocarbons add on aromatic hydrocarbons at the unsaturated bonds in the presence of BF_3 and its compounds. V. L. Vaiser [114—117] studied the reaction of acetylene in the presence of the catalyst $BF_3 . H_3PO_4$ and mercuric oxide with benzene, toluene, xylene, ethylbenzene, *iso*propylbenzene and di*iso*propylbenzene, and found that acetylene adds two molecules of each of the specified hydrocarbons and forms, with a yield of 40—55 per cent of the theoretical, ethylidenediphenyl (I), ethylidenedi-*p*-tolyl (II), ethylidenedixylyl (III), ethylidenediethylphenyl (IV), ethylidenedi*iso*propylphenylbenzene (V) and ethylidene bis-di*iso*propylphenylbenzene (VI):

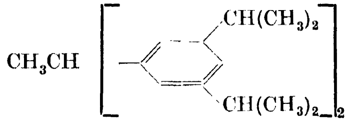
$CH_3CH(C_6H_5)_2$ (I)

$CH_3CH(C_6H_4CH_3)_2$ (II)

$CH_3CH[C_6H_3(CH_3)_2]_2$ (III)

$CH_3CH[C_6H_4(C_2H_5)_2]$ (IV)

$CH_3CH[C_6H_4CH(CH_3)_2]_2$ (V)



(VI)

Together with the main ethylidene diaryl products there are obtained in this reaction small quantities of more complex resinous substances, which are probably formed by the polymerization of the vinylaryls (styrenes) which are first formed as intermediate products. The reaction of acetylene with the specified hydrocarbons in the presence of a sulphuric acid catalyst proceeds in this way. but the yield of the corresponding ethylidene diaryls here is 2—5 times lower than with $BF_3 . H_3PO_4$ and HgO, which is seen from Table 56.

Table 56. *Alkylation of aromatic hydrocarbons with acetylene*

Aromatic hydrocarbon	Catalyst	Amount of alkylate (ml)	Amount of ethylidenearyl (ml)
Benzene	$BF_3 . H_3PO_4 + HgO$	16	10
Benzene	H_2SO_4	11	3
Toluene	$BF_3 . H_3PO_4 + HgO$	46	30
Toluene	H_2SO_4	25	15
Xylene	$BF_3 . H_3PO_4 + HgO$	32	14
Xylene	H_2SO_4	26	3

According to patent data [118], acetylene and xylene in the presence of $BF_3 . O(C_2H_5)_2$ and HgO give a fusible dimethylstyrene polymer with a yield of 82 · 3 per cent of the theoretical.

Diene hydrocarbons of the butadiene and *cyclo*pentadiene type add on aromatic hydrocarbons and form the corresponding alkenyl derivatives in the presence of the catalysts: BF_3 [119], $BF_3 . H_3PO_4$ [120], $BF_3 . H_2O$ [121, 122], $BF_3 . ROH$ or $BF_3 . RCOOH$ [123]. If, for example, 2 moles butadiene are passed into 4 moles benzene containing 50 ml $BF_3 . H_3PO_4$ at a temperature of 85—88°, butenyl benzenes are obtained in a yield of 80 per cent of the theoretical. Toluene and 1,3-pentadiene in similar conditions give pentenyl toluene.

6. DESTRUCTIVE ALKYLATION OF AROMATIC HYDROCARBONS WITH PARAFFINS

Aromatic hydrocarbons are very easily alkylated by isoparaffins in the presence of BF_3 and tertiary alkyl fluorides [124]. Thus, methyl*cyclo*hexane and benzene in the presence of *tert.*-butylfluoride and BF_3 give methyl*cyclo*hexyl benzene and *tert.*-butyl benzene. With higher isoparaffins, aromatic hydrocarbons in the presence of HF and BF_3 undergo destructive alkylation [125] similar to the destructive alkylation of *iso*butane (Chap. X). For example, benzene is alkylated by 2,2,4-trimethylpentane in the presence of HF with an addition of 5 per cent BF_3 at a temperature of 400° and increased pressure (90 atm) with the formation of a 65 per cent yield of *tert.*-butyl benzene.

Free BF_3 does not activate this reaction according to the results of Ipatiev and Grosse [126], while in the presence of $AlCl_3$ or $ZnCl_2$ it proceeds at a temperature of 25—75° and ordinary pressure with the formation of *tert.*-butyl benzenes.

Aromatic hydrocarbons are alkylated also by normal paraffins containing not less than 5 atoms of carbon in the molecule, in the presence of HF and 2—20 per cent by weight of BF_3 at a temperature of 180—400° and increased pressure [127].

7. ALKYLATION OF BENZENE AND ITS HOMOLOGUES WITH ALKYL HALIDES

The reaction of aromatic hydrocarbons with alkyl halides in the presence of $AlCl_3$ was discovered in 1877 and is known as the Friedel—Crafts reaction. This is the oldest laboratory method of preparing alkyl derivatives of aromatic hydrocarbons. But it requires a large consumption of the $AlCl_3$ catalyst, is bound up with difficulties of separating the final products, is not guaranteed practicable on the large scale with cheap raw material and has therefore not been widely used in industry.

The failure of the first attempts to use free boron fluoride as a catalyst for the Friedel—Crafts reaction led to incorrect statements that in the

Table 57. Alkylation of benzene and toluene with alkyl halides in the presence of BF_3 *and its compounds* [129]

Reagent				Catalyst (moles)	Time of heating (hr)	Yield of alkylbenzenes and alkyltoluenes (%)	
alkyl halide		hydrocarbon					
formula	moles	formula	moles			mono-	di-
$(CH_3)_3CCl$	0·8	C_6H_6	2·0	BF_3(0·13) + $(CH_3)_3COH$ (0·2)	5·0	46	10
$(CH_3)_3CCl$	1·0	C_6H_6	2·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2)	2·5	46	16
$CH_3CH_2CCl(CH_3)_2$	0·8	C_6H_6	2·0	BF_3 (0·13) + $CH_3CH_2C(OH)(CH_3)_2$	5·5	43	traces
$CH_3CH_2CCl(CH_3)_2$	1·0	C_6H_6	2·0	BF_3 (0·17) + $BF_3 . H_2O$ (0·2)	5·5	53	traces
$C_6H_5CH_2Cl$	0·8	C_6H_6	2·0	BF_3 (0·15) + $C_6H_5CH_2OH$ (0·2)	13·0	12	4
$C_6H_5CH_2Cl$	1·0	C_6H_6	2·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2)	7·5	59	2
$(CH_3)_2CHBr$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2)	9·0	18	—
$(CH_3)_2CHBr$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2) + H_2SO_4 (23 g)	8·0	50	—
$CH_3CH_2CHClCH_3$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2)	6·5	22	—
$CH_3CH_2CHClCH_3$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·2) + $BF_3 . 2H_2O$ (0·2) + H_2SO_4 (48 g)	6·5	40	—
$(CH_3)_3CCl$	0·5	$C_6H_5CH_3$	1·0	$BF_3 . 2H_2O$ (0·2)	3·5	40	—
$(CH_3)_3CCl$	0·8	$C_6H_5CH_3$	2·0	BF_3 (0·15) + $(CH_3)_3COH$ (0·2)	5·0	68	—
$(CH_3)_3CCl$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·2) + $BF_3 . 2H_2O$	2·0	66	—
$(CH_3)_3CCl$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·29) + CH_3OH (0·29)	3·0	64	—
$(CH_3)_3CCl$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·15) + CH_3COOH (0·2)	6·0	65	—
$CH_3CH_2CCl(CH_3)_2$	0·8	$C_6H_5CH_3$	2·0	BF_3 (0·14) + $CH_3CH_2C(OH)(CH_3)_2$ (0·2)	6·0	52	—
$CH_3CH_2CCl(CH_3)_2$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·13) + $BF_3 . 2H_2O$ (0·2)	5·0	66	—
$CH_3CH_2CHBrCH_2CH_3$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·14) + $CH_3CH_2CH(OH)CH_2CH_3$ (0·15)	5·5	12	—
$CH_3CH_2CHBrCH_2CH_3$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·19) + $BF_3 . 2H_2O$ (0·2)	5·0	17	—
$CH_3CH_2CHBrCH_2CH_3$	0·5	$C_6H_5CH_3$	1·0	BF_3 (0·11) + $BF_3 . 2H_2O$ (0·2) + H_2SO_4 (20 g)	10·0	58	—
$C_6H_5CH_2Cl$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·15) + $BF_3 . 2H_2O$ (0·2)	5·0	70	5
$CH_2{=}CHCH_2Cl$	1·0	$C_6H_5CH_3$	2·0	BF_3 (0·58) + $BF_3 . 2H_2O$ (0·58)	8·0	14	—

presence of BF_3 it is impossible to obtain good results in the alkylation of aromatic hydrocarbons by alkyl halides [128]. However, Hennion and Kurtz [129] showed that if BF_3 is used with a small quantity of water, alcohols or other polar compounds, the alkylation of aromatic hydrocarbons by alkyl halides proceeds quickly and with a good yield of alkyl-substituted aromatic hydrocarbons.

This reaction was well studied on benzene and toluene. It was shown that benzene and toluene are more easily alkylated by tertiary alkyl halides and benzyl chloride. Secondary alkyl halides give a comparatively low yield of alkylated products, but it may be increased if H_2SO_4 is added to aqueous BF_3. Normal primary alkyl chlorides and bromides at atmospheric pressure hardly alkylate aromatic hydrocarbons in the presence of boron fluoride. According to patent data [96, 97] benzene and ethyl bromide in the presence of BF_3, as with other catalysts, on heating to 250° in an autoclave for 3 hr form an oil with b. p. 90—200°. A higher boiling oil is obtained when benzene is alkylated with chlorinated paraffins [130].

In the alkylation of toluene and other monoalkyl benzenes the alkyl radical usually enters in the *p*-position. As a rule, only one alkyl radical enters into the benzene ring, and if dialkyl derivatives are formed, they are formed in very small amounts, which is evident from Table 57 [129].

Investigation of the reaction of toluene with *cyclo*hexyl halides showed that BF_3 does not activate the cyclohexylation of toluene with *cyclo*hexyl bromide, but is a very active catalyst for the cyclohexylation of toluene by *cyclo*hexyl fluoride [131]. This sharp difference of catalytic activity of BF_3 is probably connected with the comparatively high stability of the BF_4^- ion formed, in comparison with the BF_3Cl^- or BF_3Br^- ions.

8. ALKYLATION OF BENZENE AND ITS HOMOLOGUES WITH ALCOHOLS

The alkylation of aromatic hydrocarbons by alcohols has been known since the last century. It may be carried out with primary, secondary and tertiary alcohols with the same catalysts that are used in the alkylation of aromatic hydrocarbons with other reagents.

Alcohols react more actively than alkyl halides. Benzene, toluene and xylenes may be alkylated by propyl and butyl alcohols in the presence of 70—80 per cent H_2SO_4 at a temperature of 40—80° [132]. To obtain good yields of alkylbenzenes 10 vols. of acid should be taken for 1 vol. of hydrocarbon. Hydrogen fluoride has a high catalytic activity in the given reaction [133], especially in the alkylation of benzene with secondary and tertiary alcohols.

In the U.S.S.R. I. P. Tsukervanik and collaborators [134—136] successfully develop the synthesis of alkylbenzenes in this direction. In a series of investigations they showed that aromatic hydrocarbons are alkylated by alcohols in the presence of 1—2 moles of $AlCl_3$ per 1 mole of the hydrocarbon with an 80—90 per cent yield of the alkyl benzenes. The alkylation of benzene and toluene by tertiary alcohols in the presence of $FeCl_3$ (1—2 moles per 1 mole alcohol) gives alkyl benzenes in a yield of 70—95 per cent, and by secondary alcohols in a yield of 38—75 per cent [137].

A substantial disadvantage of the catalysts enumerated is the necessity of using large amounts of them for the preparation of good yields of alkylbenzenes. The search for more active catalysts for the described reaction has therefore not been abandoned even at the present time. From this point of view boron fluoride has a certain interest as a catalyst.

First McKenna and Sowa [138] studied the catalytic action of boron fluoride in the alkylation of benzene and its homologues by alcohols and showed that an equimolecular mixture of the reagents in the presence of BF_3 gives a mixture of mono-, di- and polyalkyl benzenes on heating to 60° for 6 hr. Moreover, normal primary and secondary alcohols give secondary alkyl benzenes, and tertiary alcohols give tertiary alkyl benzenes.

The dialkyl benzenes are mainly the *p*-isomers with an admixture of negligible amounts of the *o*-derivatives [139].

The ease of alkylation of benzene with alcohols occurs in relation to the property of the latter to be dehydrated. The alkylation is therefore appreciably accelerated by the addition of substances such as P_2O_5, H_2SO_4 or $C_6H_5SO_3H$ [140, 141], especially in alkylation by primary alcohols which split off water with the utmost difficulty in the absence of dehydrating agents. Thus, benzene (0 · 5 mole) is not alkylated on heating for 4 hr with *n*-butyl alcohol (0 · 5 mole) in the presence of BF_3 (0 · 5 mole), but after the addition of P_2O_5 (0 · 12 mole) to this mixture and heating for 3 hr, *sec.*-butylbenzene is formed in a yield of 73 per cent and *p*-di-*sec.*-butylbenzene in a yield of 8 per cent. If 100 per cent H_2SO_4 (0 · 5 mole) is added instead of P_2O_5, *sec.*-butylbenzene is also obtained in 37 per cent yield, but on heating the mixture for 4 hr with benzene sulphonic acid (0 · 5 mole) the yield of *sec.*-butylbenzene amounts to 63 per cent.

A. V. Topchiev, G. M. Yegorova and V. N. Vasilieva [142] studied the alkylation of benzene by propyl and butyl alcohols in the presence of the catalyst $BF_3 . H_3PO_4$ and showed that this catalyst is also very active in the given reaction and enables alkyl benzenes to be obtained with a total yield of more than 80 per cent. The main products of the reaction are monoalkylbenzenes. With excess of benzene the di-substituted ones amount to about 5 per cent. When the relative quantity of alcohol is increased, the yield of dialkylbenzenes increases. The most satisfactory conditions of alkylation by *iso*propyl alcohol are: *iso*-$C_3H_7OH : C_6H_6 : BF_3 . H_3PO_4 = 0 \cdot 5 : 1 : 0 \cdot 5$, heating the mixture for 2—3 hr to 95° and good stirring. A decrease in the amount of catalyst from 0 · 5 to 0 · 25 mole reduces the yield of alkylation products from 76—81 to 28—39 per cent. Some characteristic results are given in Table 58 [142].

Table 58. *Alkylation of benzene with* iso*propyl alcohol in the presence of* $BF_3 . H_3PO_4$ [142]

Molar ratio alcohol : benzene : catalyst	Conditions of reaction		Yield of *iso*propylbenzene (%)		
	time (hr)	temperature (°C)	mono-	di-	total
0·5 : 1·0 : 0·5	2	97	75·0	7·3	82·3
0·5 : 1·0 : 0·5	3	95	72·0	4·2	76·2
0·5 : 1·0 : 0·5	4	97	69·7	4·4	74·1
1 : 1 : 1	—	95	48·3	22·1	70·4
0·5 : 2 : 0·5	—	86	76·6	4·9	81·5

When benzene is alkylated by optically active D-*sec.*-butyl alcohol in the presence of BF_3 L-*sec.*-butyl benzene is obtained in 48 per cent yield [143]. Whether such a conversion takes place by means of optical inversion or racemization has not yet been established, but in connection with this it may be observed that if this reaction is carried out in the presence of $AlCl_3$, almost exclusively D, L-*sec.*-butylbenzene is formed in a yield of 49 · 7 per cent.

Benzene and its homologues are alkylated also by higher alcohols: *n*-amyl, *n*-octyl, *n*-decyl and *n*-dodecyl in the presence of BF_3 with P_2O_5, H_2SO_4, $C_6H_5SO_3H$ and B_2O_3 [144, 145].

Benzyl alcohol and benzene with BF_3 form diphenylmethane, *p*-dibenzylbenzene and polybenzylbenzenes with a yield of 23 · 2, 15 · 1 and 34 · 0 per cent respectively [138]. According to A. V. Topchiev's data [146], the benzylation of benzene by benzyl alcohol in the presence of $BF_3 . H_3PO_4$ gives diphenylmethane in 32 · 1 per cent yield, i.e. in a larger yield than with the catalyst BF_3. *cyclo*Hexanol and benzene form mono-, di- and poly*cyclo*hexylbenzenes with a yield of 56 · 2, 27 · 4 and 6 · 4 per cent respectively [138]. Benzene and decalol in the presence of $BF_3 . H_3PO_4$ give the corresponding phenyldecalins [146]. Allyl alcohol alkylates benzene to allylbenzene (8 · 7 per cent) and higher boiling products (31 per cent), among which considerable quantities of diphenylpropane are found. The latter may be obtained by reacting allylbenzene with benzene.

According to Welsh and Hennion's data [147], in the alkylation of toluene and ethylbenzene with different alcohols in the presence of BF_3 and P_2O_5 the alkyl radical enters into the *para*-position and *p*-dialkylbenzenes are mainly formed. Serijan [148] studied in detail the alkylation of toluene by *tert.*-butyl alcohol in the presence of BF_3 and $AlCl_3$, using approximately the same conditions as Welsh and Hennion, and by accurate distillation of the alkylation products with a fractionating column with an efficiency of 100 theoretical plates showed that in the reaction with the catalyst BF_3 *p*- and *m-tert.*-butyltoluenes are formed in approximately equal quantities, but when $AlCl_3$ is used the *m*-isomer is obtained in considerably larger quantities than the *p*-isomer. With regard to the *o*-isomer, it was not detected even in traces. It is assumed that the product obtained by Welsh and Hennion, and taken by them to be *p-tert.*-butyltoluene, is also a mixture of the *p*- and *m*-isomers which are difficult to separate by ordinary fractionation on account of the very close boiling points. For greater conclusiveness the properties of the three isomeric *tert.*-butyltoluenes obtained by Serijan and collaborators (the *o*-isomer for comparison was obtained by another method), and the product isolated by Welsh and Hennion are given in Table 59.

Table 59. Physico-chemical constants of tert.*-butyltoluenes*

Properties	Serijan' s *tert.*-butyltoluene			Welsh and Hennion's *p-tert.*-butyltoluene
	o-	*m*-	*p*-	
m. p. (°C)	—50·32	—41·39	—52·49	—
b. p. (°C)	200·45	189·29	192·75	188—189
d^{20}	0·88976	0·86587	0·86115	0·8641
n_D^{20}	1·50766	1·49456	1·49115	1·4929
Yield with BF_3 (%)	—	28	23	—
Yield with $AlCl_3$ (%)	—	34	14	—

Xylenes are alkylated by alcohols in the presence of BF_3. *o*-Xylene with *tert.*-butyl alcohol forms 1,2-dimethyl-4-*tert.*-butylbenzene [149]. *m*-Xylene with *sec.*-butyl and *tert.*-butyl alcohols in the presence of BF_3 forms 1,3-dimethyl-4-*sec.*-butylbenzene and 1,3-dimethyl-5-*tert.*-butylbenzene respectively [150]. With *p*-xylene a mixture of alkylation products which are difficult to separate is obtained.

Boron fluoride with P_2O_5 is also an active catalyst for the alkylation of mono- and di-halobenzenes with alcohols, and in contrast to $AlCl_3$ which directs the alkyl radicals into the *o*-, *m*- and *p*-positions [151], with boron fluoride mainly *p*-alkylhalobenzenes are obtained, which is demonstrated by their conversion by oxidation into *p*-halobenzoic acid.

In the alkylation of chloro-, bromo- and iodobenzenes with propyl, butyl, amyl and octyl alcohols [152] the yields of alkylhalobenzenes decrease according to the increase of molecular weight of the halobenzenes and alcohols and increase as the alcohols have a greater tendency to dehydration.

Of the dihalobenzenes, meanwhile, the propylation of *o*-dichlorobenzene with *iso*propyl alcohol in the presence of BF_3 and P_2O_5 has been studied [153].

Bachman and Hellman [154] carried out a very interesting haloalkylation of benzene, toluene, *iso*propylbenzene and their derivatives with halohydrins. If halohydrins with a hydroxyl group on the secondary and a halide on the primary carbon atoms are taken, for example $CH_3CH(OH)CH_2Cl$, the reaction proceeds exclusively at the expense of the alcohol group with the formation of haloalkylbenzenes with a yield of 30—50 per cent. In addition monoalkylbenzenes react more easily than benzene, and chiefly form *p*-haloalkyl substituted benzenes. Free BF_3 appears to be sufficiently active as a catalyst, but the addition of dehydrating agents (H_2SO_4 or P_2O_5) to it increases the yield of products by 5—10 per cent.

By splitting off hydrohalic acids from the compounds obtained the authors prepared 16 α-methylstyrenes and studied their copolymerization with butadiene, methylmethacrylate and maleic anhydride.

The most common procedure for the reported new synthesis of α-methylstyrenes in the presence of the catalyst BF_3 is the following. A cooled and well stirred solution of 1920 g (15 moles) *o*-chlorophenol and 520 g (5 · 5 moles) freshly distilled propylene chlorohydrin is saturated with boron fluoride at a temperature below 10° and 196 g (1 · 4 moles)

Table 60. *Alkylhalogenation of aromatic compounds* [154]

Reagent		Yield of alkylation products (%)
Halohydrin	Aromatic compound	
$CH_3CH(OH)CH_2Cl$	C_6H_6	37
$CH_3CH(OH)CH_2Cl$	$C_6H_5CH_3$	36
$CH_3CH(OH)CH_2Cl$	C_6H_5Cl	29
$CH_3CH(OH)CH_2Cl$	$C_6H_5CH(CH_3)_2$	48
$CH_3CH(OH)CH_2Cl$	*o*-Xylene	27
$CH_3CH(OH)CH_2Cl$	*o*-Chlorotoluene	30
$CH_3CH(OH)CH_2Cl$	*o*-Bromotoluene	30
$CH_3CH(OH)CH_2Cl$	*o*-Dichlorobenzene	7
$CH_3CH(OH)CH_2Cl$	Anisole	5
$CH_3CH(OH)CH_2Cl$	2,6-Dichlorotoluene	4
$CH_3CH(OH)CH_2Cl$	1-Chloronaphthalene	20
$CH_3CH(OH)CH_2Br$	$C_6H_5CH(CH_3)_2$	32
$CH_3CH(OH)CH_2Br$	*o*-Chlorotoluene	17
$CH_3CH_2CH(OH)CH_2Cl$	$C_6H_5CH_3$	41
$CH_3CH_2CH(OH)CH_2Br$	$C_6H_5CH_3$	51

P_2O_5 is added. The heterogeneous mixture formed is heated at 75° for 4 hr. Meanwhile the BF_3 is distilled off and collected in a trap (with water). The mixture is cooled, and the upper layer is washed with water, dried and distilled with an efficient column. The yield of product is 358 g or 32 per cent.

Results of the alkylation of aromatic compounds by halohydrins are given in Table 60.

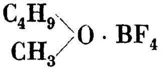
The presence of a large number of original investigations on material of this class with almost complete absence of patent literature attracts attention.

9. ALKYLATION OF BENZENE AND ITS HOMOLOGUES WITH ETHERS AND ESTERS

The possibility of alkylating aromatic hydrocarbons with ethers in the presence of boron fluoride arises from the property of these ethers of forming coordination compounds with BF_3 which split up into olefines and alcohols [155]. The alkylation of benzene with ethyl, *iso*propyl, *iso*amyl, *iso*propylphenyl, ethylbenzyl, *n*-propylbenzyl and dibenzyl ethers has been well studied [155, 157]. In carrying out the reaction it is recommended that 2 moles benzene and $0 \cdot 5-1$ mole BF_3 for 1 mole ether be used [156]. As a result of the alkylation mono-, di- and polyalkylbenzenes are obtained. The dialkylbenzenes are mainly *p*-isomers with the addition of small quantities of *o*-isomers, the formation of which only Serijan disputes [148]. *iso*Propyl and benzyl ethers are particularly vigorous alkylating agents. With *n*-propylbenzyl ether benzyl benzenes are formed [157].

Ethylene, propylene and butylene oxides, which may be considered as cyclic ethers, on reacting with aromatic hydrocarbons in the presence of BF_3 form aromatic alcohols. Benzene with ethylene oxide gives phenylethyl alcohol, and is partly converted into dibenzyl [158].

Many investigators consider that boron fluoride without activators cannot be an effective catalyst for organic reactions. The work of Burwell and Elkin is interesting in this connection [159]. These authors studied the alkylation of benzene with *sec.*-butylmethyl ether in the presence of BF_3 in a ratio of 7 : 1 : 1, and showed that if the reagents and catalyst were well dried and placed in a reaction vessel excluding the entry of moisture from the atmosphere, no reaction would occur during three weeks. But it is sufficient to add to this reaction mixture a little water to make the process of alkylation immediately set in with the formation of *sec.*-butylbenzenes exclusively. Toluene was not observed even in traces. Sulphuric acid, chlorosulphonic acid and ethane sulphonic acid are still more effective activators of boron fluoride in this reaction.



Thus, the coordination compound *sec.*- $\left.\begin{matrix}C_4H_9\\CH_3\end{matrix}\right\rangle O \cdot BF_4$ at room temperature is probably very stable, and in order to split it up into olefine or carbonium ion the presence of compounds forming proton complexes with BF_3 is necessary.

Benzene can be alkylated by several esters of organic and mineral acids [160]. Moreover, depending on the ester taken, the reaction proceeds at room or increased temperature. Normal and *sec.*-butyl esters of formic and acetic acids with benzene give one and the same *sec.*-butylbenzene. *iso*Butyl formate gives *tert.*-butylbenzene. Normal alkyl esters react with more difficulty than esters having radicals of *iso*-structure, which completely agrees with their smaller tendency to dissociate into olefine and acid. The dialkylbenzenes formed also in the given case are mainly the *para*-isomers. Vinyl acetate with benzene forms a mixture of resinous products which is difficult to identify.

10. ALKYLATION OF NAPHTHALENE AND OTHER POLYCYCLIC AROMATIC HYDROCARBONS

Naphthalene may be alkylated by olefines, alkyl halides, alcohols and ethers in the presence of the catalysts H_2SO_4, H_3PO_4, HF, $AlCl_3$, $FeCl_3$ and BF_3.

There are no original investigations on the alkylation of naphthalene with olefines in the presence of the catalyst BF_3. According to patent data naphthalene and hydronaphthalenes are alkylated by ethylene [93, 96, 97], propylene [75, 87, 102] and polymerization products of olefines [82, 161, 162] in the presence of BF_3, but still better in that of its coordination compounds with mineral acids or with water, with the formation of the corresponding mono- and di-alkylnaphthalenes. In the alkylation of naphthalene with ethylene in the presence of BF_3 and HCl mono- and poly-ethyl naphthalenes are formed [96, 97]. In the alkylation of naphthalene with propylene in the presence of BF_3 a mixture of *iso*propyl naphthalenes is obtained, boiling within the limits 140—200° at 10 mm, and polymerization products of propylene [102]; with the catalyst $BF_3 + H_2SO_4$ in carbon tetrachloride mainly β-*iso*propylnaphthalene of b.p. 260—270° is formed [75]; with the catalyst $BF_3 . H_3PO_4$ in *cyclo*hexene β-*iso*propylnaphthalene is obtained in almost theoretical yield [87].

Naphthalene, methyl naphthalene, anthracene, phenanthrene, pyrene and carbazole are alkylated by polymerization products of olefines, for example by dodecylene (obtained by the polymerization of propylene) in the presence of $BF_3 . H_2O$ [82].

Naphthalene and *cyclo*hexene in the presence of BF_3 give β-*cyclo*hexylnaphthalene [163].

If naphthalene is dissolved in *iso*propyl, *tert.*-butyl, *cyclo*hexyl or benzyl alcohols and the solutions are saturated with boron fluoride at a temperature of 25°, monoalkylnaphthalenes are chiefly obtained. The alkyl radical enters preferably into the β-position and only in the case of the alkylation of naphthalene with benzyl alcohol or *n*-propylbenzyl ether are α-benzylnaphthalenes obtained [157, 163].

Naphthalene may be alkylated by higher alcohols in the presence of BF_3 with P_2O_5, H_2SO_4 or $C_6H_5SO_3H$ [144]. To carry out the reaction it s recommended that P_2O_5 be added quickly with shaking to an alcohol, for example octyl, cooled to 0°, and then naphthalene added and BF_3 passed into the mixture at 0—10° for 2 · 5 hr or at 90—95° for 1 · 5 hr. The most characteristic data on the alkylation of naphthalene by alcohols are summarized in Table 61.

Table 61. *Alkylation of naphthalenes with alcohols* [144, 163]

Reagent				Alkylation product	Yield (%)
Hydrocarbon	Moles	Alcohol	Moles	Name	
Naphthalene	0·4	*iso*Propyl	0·6	β-*iso*Propylnaphthalene	35
Naphthalene	0·4	*iso*Propyl	1·6	Tri*iso*propylnaphthalene	57
Naphthalene	0·4	*tert.*-Butyl	1·0	β-*tert.*-Butylnaphthalene	62
				Di-*tert.*-butylnaphthalene	5
Naphthalene	0·4	*cyclo*Hexanol	0·45	β-*cyclo*Hexylnaphthalene	63
				Di-*cyclo*hexylnaphthalene	9
Naphthalene	0·4	Benzyl	0·45	α-Benzylnaphthalene	28
				β-Benzylnaphthalene	2
				Dibenzylnaphthalene	15
				Tribenzylnaphthalene	20
Naphthalene		*n*-Propylbenzyl ether		α-Benzylnaphthalene	48
Naphthalene	78 g	Octyl	200 g	Octylnaphthalene	36·7
				Dioctylnaphthalene	29·8
Naphthalene		Dodecyl		Dodecylnaphthalene	23·4
2-Methyl-naphthalene		*n*-Octyl		Octyl-2-methylnaphthalene	20·8
				Dioctyl-2-methylnaphthalene	39·2
Tetralin		Decyl		Decyltetrahydronaphthalene	63·8

Boron fluoride etherates may be alkylating agents for naphthalene. If naphthalene (0 · 25 mole) and $BF_3 . O(CH_3)_2$ (1 mole) are heated, for example, under a reflux condenser for 40 hr, mono- and di-methylnaphthalenes are obtained [163].

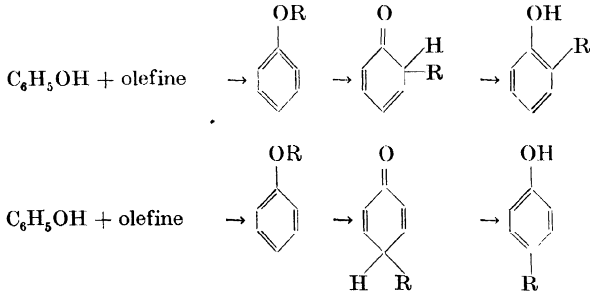
There are indications that naphthalene is alkylated by the chlorination products of benzine [130], and α-chloronaphthalene by propylene glycol chlorhydrin [154] in the presence of boron fluoride.

11. ALKYLATION OF PHENOLS AND THEIR DERIVATIVES

Alkyl phenols and their ethers have been widely used in very different branches of the national economy. They are obtained by the catalytic alkylation of phenols and their ethers with olefines, alkyl halides, alcohols and ethers.

Alkylation of Phenols with Olefines

The alkylation of phenols with olefines is without doubt the simplest and most perspective synthesis of alkylphenols and their ethers. It may be considered as an addition reaction of phenol to an olefine according to V. V. Markovnikov's rule with subsequent isomerization of the alkylphenyl ethers thus formed to *o*- or *p*-derivatives of quinoid structure, and regrouping of the latter into more stable alkyl phenols according to the scheme:



Alkyl phenyl ethers are alkylated by olefines by the direct entry of the alkyl radical into the benzene ring. Thus, phenols are probably also alkylated at increased temperatures.

The catalysts generally used (metal halides and mineral acids) for the alkylation of phenols with olefines possess the substantial disadvantage that they give rise to various side reactions and thus lower the efficiency of the process.

The use of boron fluoride and its compounds with ethyl ether and orthophosphoric acid as catalysts for the alkylation of phenols, halophenols, nitrophenols, alkylphenyl ethers and thiophenol by olefines was studied by S. V. Zavgorodnii [164—168]. It was shown by him that the alkylation of phenols by normal olefines in the presence of $BF_3 . O(C_2H_5)_2$ takes place more easily than the alkylation of hydrocarbons, and is not accompanied by side reactions. Depending on the conditions, the final products obtained are alkylphenols or their alkyl ethers, but more often a mixture of both. The proportion of products of ethereal and phenolic character and their total yield depend on the chemical nature of the reagents, temperature, time of reaction, presence of solvents and other factors.

Ethylene with phenol in the presence of 5 per cent by volume of BF_3 and 2 per cent HCl at a temperature of 150—300° and pressure of 50 atm forms phenetole [169]. Cresol and phenol in the presence of BF_3 give ethyltolyl ether [97]. The formation of ethylphenyl ethers in the specified conditions and the absence of ethylphenols is explained by the high stability of these ethers.

The alkylation of phenol with propylene in the presence of BF_3, as Nieuwland and collaborators found [170], proceeds through a series of condensations and isomerizations according to the following scheme:

(I) $C_6H_5OH + CH_3CH = CH_2 \rightarrow C_6H_5OC_3H_7$ *iso*propylphenyl ether
(II) $C_6H_5OC_3H_7 \xrightarrow[\text{zation}]{\text{isomeri-}} HOC_6H_4C_3H_7$ *o*-*iso*propylphenol
(III) $HOC_6H_4C_3H_7 + CH_3CH = CH_2 \rightarrow H_7C_3OC_6H_4C_3H_7$ *o*-*iso*propylphenyl*iso*propyl ether
(IV) $H_7C_3OC_6H_4C_3H_7 \xrightarrow[\text{zation}]{\text{isomeri-}} HOC_6H_3(C_3H_7)_2$ 2,4-di*iso*propylphenol
(V) $HOC_6H_3(C_3H_7)_2 + CH_3CH = CH_2 \rightarrow H_7C_3OC_6H_3(C_3H_7)_2$ 2,4-di*iso*propylphenyl*iso*propyl ether
(VI) $H_7C_3OC_6H_3(C_3H_7)_2 \xrightarrow[\text{zation}]{\text{isomeri-}} HOC_6H_2(C_3H_7)_3$ 2,4,6-tri*iso*propylphenol
(VII) $HOC_6H_2(C_3H_7)_3 + CH_3CH = CH_2 \rightarrow H_7C_3OC_6H_2(C_3H_7)_3$ 2,4,6-tri*iso*propylphenyl*iso*propyl ether

The predominance of these or other products in this reaction depends on the amounts of propylene and catalyst, and chiefly on the temperature. At 0° reaction (I) predominates and partially reaction (II) takes place. At 20° the product of reaction (I) is present in very small quantities, because the reaction proceeds mainly according to equations (III) and (IV). But at 40° principally tri*iso*propylphenol and its *iso*propyl ether are obtained.

Phenol and pseudobutylene in the presence of $BF_3 . O(C_2H_5)_2$ at a temperature of from —10 to —5° after 72 hr form a mixture of ethereal and phenolic products with a total yield of 81 per cent. At room temperature and with the same proportions of reagents and quantities of catalyst the yield of alkylation products increases and after 24 hr reaches 90 per cent [164]. The increase in yield occurs mainly at the expense of the formation of phenolic compounds.

A decrease in the amount of catalyst from 10 to 5·5 per cent, other conditions being equal, lowers the total yield of alkylation products as a result of the decrease in the amount of phenolic compounds. An increase of temperature to 53° enables the reaction to be completed in 3—5 hr.

p-Cresol, in contrast to phenol, is not alkylated by pseudobutylene in the presence of $BF_3 . O(C_2H_5)_2$ at room temperature. If 14 g *p*-cresol, 17 · 3 g pseudobutylene and 2 · 2 g boron fluoride ethyl etherate are heated for 2 hr on a boiling water bath, ethereal products are obtained with a yield of 64 per cent. Part of the *p*-cresol is unchanged.

The reaction of *p*-cresol with pseudobutylene in the presence of the catalyst $BF_3 + H_3PO_4$ proceeds very energetically. If 14 g *p*-cresol is added to 5 ml 75 per cent H_3PO_4 saturated with boron fluoride, 7 · 3 g pseudobutylene is added with good cooling, and then the reaction mixture is shaken and put quickly again into a cooling ice bath, the reaction begins immediately and proceeds so vigorously that the mass boils, and the reaction tube is filled with dense white fumes. In 10—20 min the reaction comes to an end, and the mixture becomes viscous. After appropriate treatment 14 · 27 g, or 67 per cent of ethereal products is obtained and 3 g unreacted *p*-cresol. The ethereal compounds are *p*-cresol *sec.*-butyl ether and *o*-*sec.*-butyl-*p*-cresol-*sec.*-butyl ether.

The reaction of phenol with pentene-2, as also the reaction with pseudobutylene, in the presence of $BF_3 . O(C_2H_5)_2$ leads to the formation of a mixture of ethereal and phenolic compounds [165]. At room temperature, merely *sec.*-amylphenyl ether is obtained, and *sec.*-amylphenols amount to 14 per cent of the total yield of alkylation products. If 23 · 5 g phenol, 3 ml $BF_3 .O(C_2H_5)_2$ and 26 · 5 g pentene-2 are allowed to react for 72 hr at room temperature 27 g, or 68 per cent of the theoretical yield, of ethereal products are obtained. The yield of phenolic compounds is 4 · 4 g or 11 per cent. The total yield of alkylation products is equal to 79 per cent.

Heating the same quantities of reagents and catalyst to 52—53° for 26 hr gives 15 · 9 g of ethereal products (yield 40 per cent) and 22 · 4 g of phenolic products (yield 56 per cent). Consequently the rise of temperature increases the total yield of alkylation products in the first place at the expense of the increase in yield of phenolic compounds.

The Alkylation of o- *and* p-*Chlorophenols with Pseudobutylene and Pentene*-2

o-Chlorophenol and pseudobutylene in equimolecular proportions in the presence of 16 per cent $BF_3 . O(C_2H_5)_2$ at room temperature form ethereal products with a yield of 54 per cent and phenolic products with a yield of 15 per cent. The ethereal products are mainly *o*-chlorophenol *sec.*-butyl ether, and the phenolic *sec*-.butyl-*o*-chlorophenol.

Heating the specified reagents taken in a 1 : 1 ratio in the presence of 13 per cent $BF_3 . O(C_2H_5)_2$ on a boiling water bath for 2 hr gives a mixture of ethereal and phenolic compounds with a yield of 52 and 24 per cent respectively. However, when the reaction is carried out in these conditions the ethereal products contain, in addition to *o*-chlorophenol *sec.*-butyl ether, *sec.*-butyl-*o*-chlorophenol, *sec.*-butyl ether and probably more complex compounds which remain in the distillation flask. The phenolic compounds contain mainly *sec.*-butyl-*o*-chlorophenol [166, 167].

Heating *o*-chlorophenol with pseudobutylene in a 1 : 2 ratio in the presence of 8 per cent $BF_3 . O(C_2H_5)_2$ at a temperature of 100° for 6 hr gives ethereal and phenolic products with a yield of 36 and 8 per cent respectively.

p-Chlorophenol [166, 167] is more reactive than *o*-chlorophenol and on reacting with pseudobutylene in equimolecular proportion in the presence of 13—15 per cent $BF_3 . O(C_2H_5)_2$ at 100° it forms a mixture of ethereal and phenolic alkylation products with a higher yield, in which in the given case ethereal compounds are chiefly obtained, the maximum yield of which (71 per cent) is reached when the mixture is heated for 4 hr. The yield of phenolic products amounts to 15—17 per cent.

The reaction of *p*-chlorophenol with pseudobutylene in 2 : 1 ratio, other conditions being equal, also gives the maximum yield of ethereal products of about 71 per cent, calculated on pseudobutylene. In 1 : 2 ratio the process of alkylation is retarded, and the yield of ethereal products falls to 61 per cent as in the reaction with *o*-chlorophenol.

The alkylation of *o*- and *p*-chlorophenols with pentene-2 was studied in the presence of 5—7 per cent of the catalyst $BF_3 . O(C_2H_5)_2$ at room temperature and at 100° with different proportions of reagents [168]. In the given case a mixture of ethereal and phenolic products is also obtained, the relative quantities of which depend on the temperature, duration of the reaction and ratio of the starting materials. As a rule, increase of temperature from room to 95—97° accelerates the alkylation. For example, in the reaction of *o*-chlorophenol with pentene-2 in equimolecular proportion an almost identical yield of ethereal compounds (32 per cent) is obtained at room temperature in 5 days and at 96—97° in 4 hr.

Higher olefines alkylate phenols in the presence of BF_3. The alkylation by tertiary olefines proceeds particularly vigorously. Here the main products are *p-iso*alkylphenols. Phenol, dissolved in pentane and treated with gaseous *iso*butylene in the presence of 70—90 per cent H_3PO_4 saturated with BF_3, gives *p-tert.*-butylphenol with a yield of 80 per cent [171]. *m*-Cresol in similar conditions gives *tert.*-butyl-*m*-cresol [171]. Phenol and di*iso*butylene with BF_3 give *tert.*-octylphenol and partly di-*tert.*-octylphenol [172—175]. *p*-Cresol and di*iso*butylene give 2-*tert.*-octyl-4-methylphenol and 2,6-di-*tert.*-octyl-4-methyl phenol [176, 177].

Phenols are alkylated by the polymerisation products of olefines in the presence of $BF_3 . nH_2O$, particularly by *iso*dodecylene obtained by the polymerization of propylene, with the formation of dodecylphenol, or by tetradecylene with the formation of tetradecylphenol [161].

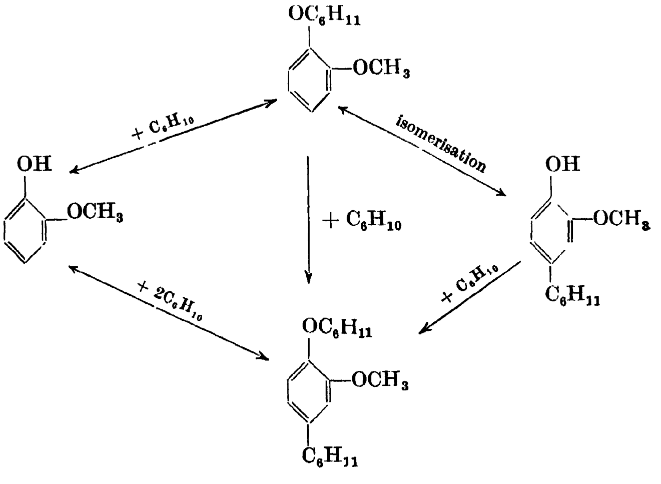
Cycloalkylation of Phenols with cyclo*Hexene*

Phenol and *cyclo*hexene in the presence of free boron fluoride in carbon disulphide solution [178] or without a solvent [179, 180] form mono-, di- and tri*cyclo*hexylphenols exclusively.

o-Cresol with *cyclo*hexene in the presence of BF_3 at 30° forms *cyclo*hexyl ether and *cyclo*hexyl-*o*-cresol with yields of 37 and 21 per cent respectively, but at 150° the ethereal products are present only in traces [178]. Guaiacol and *cyclo*hexene in 1 : 1 ratio in the presence of 5 per cent $BF_3 . O(C_2H_5)_2$ do not enter into reaction over 10 days, and the *cyclo*hexene is quantitatively regenerated. Heating the reagents in the presence of the same amount of catalyst on the boiling water bath for 4 hr gives the *cyclo*hexyl ether of guaiacol and *cyclo*hexylguaiacol 3·7 : 1 ratio with a total yield of 88 per cent. Increasing the time of heating to 12 hr increases the total yield of reaction products to 94 per cent mainly at the expense of the phenolic compounds.

It is characteristic that in the conditions described only one phenolic product, *p*-*cyclo*hexylguaiacol, is obtained. Among the ethereal compounds are found two *cyclo*hexyl ethers of guaiacol, a liquid one and a crystalline one [181].

Thus, the reaction, like the one with olefines, may be so represented that first the guaiacol through its hydroxyl group unites with the *cyclo*hexene at the double bond and forms the *cyclo*hexyl ether of guaiacol, which then either reacts again with one molecule of *cyclo*hexene and forms the *cyclo*hexyl ether of *cyclo*hexylguaiacol, or isomerizes to *cyclo*hexylguaiacol, and the latter combines with a new molecule of *cyclo*hexene and gives the *cyclo*hexyl ether of *cyclo*hexylguaiacol:



The reaction of *o*-chlorophenol with *cyclo*hexene was studied at temperatures of 16—20° and 70—95° and with different ratios of reagents in the presence of 3—4 per cent $BF_3 . O(C_2H_5)_2$ [182]. The same results are obtained with 15 days reaction at room temperature and with 2 hr heating at about 97°. Increase of the time of heating to 8 hr also increases the yield of alkylation products. However, increase of temperature and more prolonged heating favours a more intensive polymerization of *cyclo*hexene.

It should be observed that at a temperature of about 97° and with a time of reaction of not more than 8 hr, the ethereal compounds are the only products.

At room temperature *o*-chlorophenol *cyclo*hexyl ether is formed exclusively, and the polymerization of *cyclo*hexene is hardly observed.

A twofold excess of *cyclo*hexene decreases the rate of reaction at room temperature and lowers the yield of *o*-chlorophenol *cyclo*hexyl ether from 48 to 36 per cent (for the same time of reaction). On the other hand, at 100° the yield of ethereal compounds in 8 hr increases from 73 to 79 per cent. *o*-Chlorophenol *cyclo*hexyl ether is very stable and does not undergo isomerization to *cyclo*hexyl-*o*-chlorophenol on heating for 8 hr at 120—140°.

o-, *m*- and *p*-Nitrophenols are hardly alkylated either by pseudobutylene or by *cyclo*hexene in the presence of $BF_3 . O(C_2H_5)_2$ at a temperature of about 100°. *o*-Nitrophenol does not enter into reaction even in the presence of the stronger catalyst, free boron fluoride. *p*-Nitrophenol and *cyclo*hexene form *o*-*cyclo*hexyl-*p*-nitrophenol with a yield of 5 per cent [164—168]. The reaction with pseudobutylene proceeds somewhat better, but even in this case the yield of alkylation products does not exceed 10 per cent.

When thiophenol reacts with *cyclo*hexene in the presence of 10 per cent $BF_3 . O(C_2H_5)_2$ on heating on a boiling water bath for 20 hr thiophenol *cyclo*hexyl ether is formed with a 75 per cent yield [183]. It is interesting to note that in contrast to the alkylation of phenols with olefines, when 4—5 fractions have to be separated on distilling the reaction products, in the present case the ethereal product almost completely distils at 145—146°/12 mm and is a pure individual substance giving good analytical results.

Anisole and *cyclo*hexene in the presence of BF_3 give a mixture of approximately equal quantities of *o*- and *p*-*cyclo*hexylanisoles with a total yield of 59 per cent of the theoretical [178]. Diaryl ethers, for example $C_6H_5OC_6H_5$ and *p*-$CH_3C_6H_4OC_6H_5$ with *cyclo*hexene in the presence of BF_3 form cyclohexylated diaryl ethers [184].

Alkylation of Phenol with Styrene

This reaction in the presence of BF_3 at a temperature of 70° leads to the formation of a complex mixture of products [185, 186].

Reaction of Terpenes and Phenols

In the presence of BF_3 and its coordination compounds terpenes and phenols, depending on the conditions, form terpenyl ethers of phenols, terpenylphenols or resins [187—193]. Thus, the acyclic terpenes, *allo*-cymene, ocimene, myrcene and others with phenol, cresols and naphthols in the presence of 0·5—2 per cent BF_3 form resins which are used in varnish colouring technique, and their sulphonation products are used as detergents. The cyclic terpenes (pinenes, menthenes and limonene) with phenols and BF_3 or $BF_3 . ROH$ are converted into terpenyl phenols and their ethers or resinous products. Camphene and phenols in the presence of $BF_3 . O(C_2H_5)_2$ give *iso*bornyl ethers of phenols [189]. Nopinene and dipentene with 2,4-dimethylphenol and $BF_3 . O(C_2H_5)_2$ form terpene ethers of 2,4-dimethylphenol.

Reactions of Phenols with Diene Hydrocarbons

Divinyl, *iso*prene and dimethylbutadiene react comparatively easily with phenols and, depending on the catalysts and other conditions, they give either the simplest products, alkenyl derivatives, or products involving more drastic changes, compounds of high molecular weight. Polydienes of low molecular weight with phenol in the presence of boron fluoride form polyolefines with two or more phenolic residues [194]. By the reaction of hydroquinone methyl ether with dimethylbutadiene in the presence of BF_3, derivatives of chromane are obtained [195, 196]. Similarly diene hydrocarbons enter into reaction with 2-methyl-1,2-naphthoquinone in the presence of BF_3 [197].

The alkylation of phenols by acetylene in the presence of BF_3 is considered only in V. L. Vaiser's investigation [198] on the conversion of phenol, resorcinol, β-naphthol and hydroquinone in the presence of $BF_3 . H_3PO_4$ and HgO into ethylidene diphenols according to the reaction

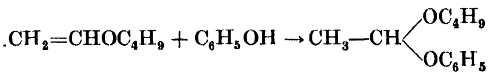
$$CH \equiv CH + HArOH \rightarrow CH_2 = CHArOH \xrightarrow{HArOH} CH_3CH(ArOH)_2$$

and in one patent according to which phenol and acetylene in the presence of $BF_3 . CH_3OH$ give vinyl phenol [199].

In some patents it is proposed to treat technical products containing phenols with olefines [95], or materials having an unsaturated character with phenols, in the presence of BF_3 [200—203] in order to impart to them definite properties or an improvement in quality. For example, the treatment of a liquid coal-tar oil containing phenol with ethylene in the presence of BF_3 is described, with the object of obtaining a product of a non-phenolic character [96], and also the treatment by phenols of linseed oil [200], natural resins and rubber [202] with the object of increasing their softening point or obtaining a thermoplastic material.

Unsaturated higher fatty acids with one or two double bonds and their esters add on phenols at the double bond in the presence of BF_3. Phenol and methyl oleate in the presence of BF_3 and HgO, on heating for 5 hr at 110°, form methyl 10-(*p*-hydroxyphenyl)-octadecanoate [204]. Similarly phenol reacts with ethyl linoleate in the presence of BF_3 [200].

Vinyl butyl ether with phenol and cresols in the presence of $BF_3 . O(C_2H_5)_2$ or $AlCl_3$, $ZnCl_2$ or $SnCl_4$ forms arylbutylacetals [205] according to the reaction



$$CH_2{=}CHOC_4H_9 + C_6H_5OH \rightarrow CH_3{-}CH\begin{cases}OC_4H_9\\OC_6H_5\end{cases}$$

Alkenylphenylalkyl ethers, for example anethole or safrole, condense with phenol in the presence of BF_3 [206]. Mono-, di- and tri-chlorodiphenyl ethers are cycloalkylated by *cyclo*hexene in the presence of BF_3 [207].

Phenoxyalkyl carboxylic acids are alkylated by olefines in the presence of BF_3 as also are alkylphenyl ethers, with direct entry of the hydrocarbon radical into the benzene ring and the formation of alkylphenoxyalkyl carboxylic acids. In the alkylation of, for example, phenoxyacetic acid with di*iso*butylene in the presence of BF_3 in the solvent CCl_4 at a temperature of 60°, *iso*octylphenoxyacetic acid is obtained [208]. On heating a mixture of phenoxyacetic acid, di*iso*heptylene and BF_3 to 125° tetradecylphenoxyacetic acid is obtained [209]. Other acids of general formula ArXRCOOH (Ar = aromatic radical; X = O or S) are also alkylated by olefines or *cyclo*-olefines in the presence of BF_3 [210]. Ethyl *p*-hydroxybenzoate with *cyclo*hexene in benzene in the presence of BF_3 on heating to 50° gives ethyl *p*-*cyclo*hexylbenzoate [211]. Free hydroxybenzoic acids are also alkylated by olefines, as described in Chapter VII.

Alkylation of Phenols with Alkyl Halides

This reaction in the presence of BF_3 has hardly been studied. There are no original investigations on this subject, and there are only indications of two patents [207, 212] about the fact that phenols or their ethers can be alkylated with alkyl halides, for example, by halogenated *cyclo*hexane in the presence of BF_3.

Alkylation of Phenols with Alcohols and Ethers

The alkylation of phenols with alcohols is the oldest method of preparing alkylphenols, having been discovered in 1881 [213]. At the present time, $AlCl_3$, $FeCl_3$, BF_3 and mineral acids, mainly H_2SO_4, $HClO_4$ and HF, are used as catalysts besides $ZnCl_2$.

The lower alcohols, methyl and ethyl, alkylate phenol in the presence of BF_3 at increased temperature under atmospheric pressure with a small yield [214]. If the alkylation is carried out at increased temperature in sealed tubes, the reaction proceeds comparatively well. With methanol, mainly anisole is formed, and with ethanol phenetole and small quantities of substituted phenols.

n-Propyl and *iso*propyl alcohols very easily alkylate phenol in the presence of BF_3 on heating with the formation of a mixture of *iso*propylphenols. The alkylation of phenol proceeds still better with *iso*butyl and *tert.*-butyl alcohols and BF_3 to *p-tert.*-butylphenol [215, 216].

2-Hydroxy-1,4-naphthoquinone and allyl alcohol in the presence of $BF_3 . O(C_2H_5)_2$ on heating for 5 hr on a water bath at 70° form 2-hydroxy-1,4-naphthoquinone allyl ether in a yield of 59 per cent of the theoretical [217]. In a similar way, from 2-hydroxy-1,4-naphthoquinone and the corresponding alcohols and $BF_3 . O(C_2H_5)_2$ 2-hydroxy-1,4-naphthoquinone *iso*propyl ether (yield 72 per cent) and 2-hydroxy-1,4-naphthoquinone methyl ether (yield 83 per cent) are obtained. Hydroxy-2-phenyl-1,4-benzoquinone with methanol and allyl alcohol in the presence of $BF_3.O(C_2H_5)_2$ forms the corresponding ethers of ?-hydroxy-2-phenyl-1.4-benzoquinone [217]. 1,4-Naphthoquinone and 1,4-naphthohydroquinone are alkylated by *iso*propyl alcohol or *cyclo*hexanol in the presence of BF_3 [218].

Mono-, di-, and trichlorodiphenyl ethers are alkylated by *cyclo*hexanol in the presence of BF_3 [207]. Phenols may be alkylated also by *tert.*-mercaptans. In the presence of 50 g. $BF_3 . C_6H_5OH$, 463 g phenol and 107 g *tert.*-C_4H_9SH at a temperature of 60° give 271 g *p-tert.*-$C_4H_9C_6H_4OH$ [219]. Primary and secondary mercaptans do not alkylate phenols in these conditions.

Phenols and their ethers are alkylated much more easily by boron fluoride etherates. If, for example, phenol or anisole is heated to boiling with boron fluoride methyl etherate, it is possible to methylate them completely to form pentamethylanisole [220]. The methylation in this case proceeds through the formation of anisole with its subsequent isomerization to methyl phenols [220]. This mechanism follows from the data of Table 62, which above all shows how the degree of methylation depends on the time of heating of the reaction mixture and on the ratio of phenol or anisole to $BF_3 . O(CH_3)_2$. When the ratio phenol : $BF_3 . O(CH_3)_2$ = 1·5 : 1, in spite of the 6 hr boiling, anisole is formed almost exclusively, and di- and polymethylated anisoles are totally absent from the reaction products, but on heating these same reagents in 1 : 5 ratio for 32 hr (experiment 5) the main reaction product is pentamethylanisole. However, even in these conditions there is 0·07 mole of anisole in the reaction products.

Table 62. Methylation of phenol and anisole with boron fluoride methyl etherate

No. of experiment	Reagent			Time of heating (hr)	Yield of methyl anisoles					
	Name	Phenolic compound (g/mole)	$BF_3 . O(CH_3)_2$ (g/mole)		Anisole (g/mole)	mono-methyl (g)	di-methyl (g)	tri-methyl (g)	tetra-methyl (g)	Penta-methyl (g/mole)
1	Phenol	47/0·5	85·5/0·75	2	28/0·26	3·0	—	—	—	—
2	Phenol	141/1·5	114/1·0	6	97·5/0·90	5·5	—	—	—	—
3	Phenol	94/1·0	208/2·0	12	32/0·30	14	5	5	10	14/0·08
4	Phenol	70·5/0·75	285/2·5	14	29/0·27	10	7	1	3	12·5/0·07
5	Phenol	94/1·0	670/5·0	32	8/0·07	13	12	3	15	78/244
6	Anisole	54/0·5	171/1·5	14	24·0/0·22	4·5	4	2	4	10/0·06
7	Anisole	27/0·25	114/1·0	19	14/0·13	4	1	1	2	6/0·03

Similarly phenol is ethylated by boron fluoride ethyl etherate [221]. On heating 4·92 g phenol and 3·46 g $BF_3 . O(C_2H_5)_2$ in a sealed tube for 12 hr on a boiling water bath, phenetole is obtained in a yield of 33·6 per cent of the theoretical [222].

Salicylic acid is alkylated by *iso*propyl, *sec*.- and *tert*.-butyl alcohols in the presence of BF_3 with the formation of esters and alkylsalicylic acids [223].

12. ALKYLATION OF HETEROCYCLIC COMPOUNDS

Boron fluoride and its coordination compounds were first used as catalysts for the alkylation of heterocyclic compounds with olefines quite recently, and mainly in the alkylation of thiophene.

There are only two patents relating to the alkylation of furan and its derivatives with olefines, and according to these furan is readily alkylated by tertiary olefines in the presence of $BF_3 . O(C_2H_5)_2$ to alkyl furans [224], and dibenzofuran with ethylene and BF_3 gives ethyldibenzofuran [225].

The first attempts of Kutz and Corson [226] to alkylate thiophene with propylene, α-butylene, *iso*butylene, amylene and *cyclo*hexene in the presence of $BF_3 . O(CH_3)_2$ and other typical alkylation catalysts were unsuccessful and led to the formation of resinous products. A deeper study of

Table 63. Alkylation of thiophene with olefines

Olefine		Catalyst		Time of reaction (hr)	Temperature (°C)	Yield of alkylthiophenes (%)		Literature reference
Name	(g)	Formula	(g)			mono-	di-	
Propylene	—	$BF_3 . O(C_2H_5)_2$	—	—	85	48	36*	[229]
Propylene	—	$SnCl_4 + CH_3NO_2$	—	—	78	14	6	[229]
β-Butylene	—	$BF_3 . O(C_2H_5)_2$	—	—	80	48	27†	[229]
β-Butylene	—	$SnCl_4 + CH_3NO_2$	—	—	65	11	2	[229]
*iso*Butylene	116	75% H_2SO_4	15	3	67	61	30	[228]
*iso*Butylene	116≠	75% H_2SO_4	15	3	67	56	41	[228]
*iso*Butylene	26	90% H_2SO_4	42	1	—10	<20	<20	[228]
*iso*Butylene	24	60% H_2SO_4	42	1	82	0	0	[228]
*iso*Butylene	117	H_2BO_2F	10	3	62	66	31	[228]
*iso*Butylene	50	$AlCl_3$	3	2	70	<10	—	[228]
*iso*Butylene	—	$SnCl_4$	—	—	50	28	33	[229]
*iso*Butylene	—	$SnCl_4 + CH_3NO_2$	—	—	50	31	17	[229]
*iso*Butylene	110	$BF_3 . O(C_2H_5)_2$	10	3	62	25	59	[228]
*iso*Butylene	110≠	$BF_3 . O(C_2H_5)_2$	10	4	62	12	77	[228]
n-Amylene	76	$BF_3 . O(C_2H_5)_2$	25	2	137	16	64	[228]
*iso*Propylethylene	—	$SnCl_4 + CH_3NO_2$	—	—	45	14	24	[229]
Trimethylethylene	—	85% H_3PO_4	—	—	70	49	12	[229]
Trimethylethylene	70	75% H_3PO_4	15	2	67	62	14	[228]
Trimethylethylene	—	85% H_3PO_4 + 96% H_2SO_4	—	—	25	78	7	[229]
Trimethylethylene	140	H_2BO_2F	20	3	62	75	14	[228]
Trimethylethylene	140	$BF_3O(C_2H_5)_2$	20	3	67	16	68	[228]
Trimethylethylene	—	$C_6H_5SO_2OH$	—	—	32	33	17	[229]
Octene-1	56	96% H_2SO_4	15	5	100	43	<20	[228]
Octene-1	112	$BF_3 . H_2O$	80	2	75	28	<72	[228]
Octene-1	—	$BF_3 . O(C_2H_5)_2$	—	—	80	56	9§	[229]
Di*iso*butylene	1120	80% H_2SO_4	120	4	35	82	7	[228]
Di*iso*butylene	1680≠	$BF_3 . O(C_2H_5)_2$	100	4	35	25	54	[228]
Di*iso*butylene	55	$AlCl_3$	1	5	47	25	52	[228]
2,2,4-Trimethylpentenes	—	BF_3	—	—	33	39	49	[229]
Di*iso*amylene	182	$BF_3 . O(C_2H_5)_2$	30	—	60	70	—	[230]
Hexadecene-1	224	$BF_3 . H_2O$	80	2	75	10	<8	[228]
*cyclo*Hexene	—	$SnCl_4 + CH_3NO_2$	—	—	51	30	14	[229]
*cyclo*Hexene	—	85% H_3PO_4 + 96% H_2SO_4	—	—	23	5	0	[229]
*cyclo*Hexene	—	$BF_3 . O(C_2H_5)_2$	—	—	80	45	18	[229]
4-Methyl*cyclo*hexene	—	$SnCl_4 + CH_3NO_2$	—	—	35	31	40	[229]
4-Methyl*cyclo*hexene	—	85% H_3PO_4	—	—	76	1	1	[229]

* Besides mono- and di-*iso*propylthiophene, tri*iso*propylthiophene was obtained with a yield of 11·2%.

† 17·5 g *β*-butylene was recovered

≠ Molar ratio, olefine : thiophene = 2 : 1.

§ 25·4% octene was recovered.

Table 63 *(continued)*

Olefine		Catalyst		Time of reaction (hr.)	Temperature (°C)	Yield of alkylthiophenes (%)		Literature reference
Name	(g)	Formula	(g)			mono-	di-	
4-Methyl*cyclo*hexene	—	85% H_3PO_4 + 96% H_2SO_4	—	—	21	20	3	[229]
α-Methylstyrene	—	85% H_3PO_4	—	—	80	54	13**	[229]
α-Methylstyrene	—	$BF_3 . O(C_2H_5)_2$	—	—	33	11	32	[229]
Bi*cyclo*pentene	—	$BF_3 . O(C_2H_5)_2$	—	—	40	31	30	[229]
Methallyl chloride	—	$BF_3 . O(C_2H_5)_2$	—	—	80	47	9	[229]
*cyclo*Propane††	—	$BF_3 . O(C_2H_5)_2$	—	—	90	39	16	[229]

** 38% α-methylstyrene was recovered.

†† 16% of the hydrocarbon C_3H_6, consisting of 30% propylene and 70% *cyclo*propane was recovered.

this reaction by many investigators [227—232] showed that thiophene and its homologues may be alkylated without any substantial decomposition and resinification by both *iso*- and normal olefines in the presence of the catalysts H_3PO_4, H_2SO_4, $AlCl_3$ and of various coordination compounds of boron fluoride with the formation of mono- and dialkylthiophenes. Particularly active catalysts for alkylation are the compounds $BF_3 . O(C_2H_5)_2$ and $BF_3 . H_2O$, as is seen from the data of Table 63, obtained in the alkylation of thiophene with olefines in molar ratio 1 : 1. In the presence of these catalysts mono- and dialkylated thiophenes are formed in almost quantitative yield. The monosubstituted derivatives are mainly 2-alkylthiophenes. The most satisfactory conditions for alkylation by *iso*-olefines are: temperature 25—85° and time from 1 to 5 hr, and by normal olefines: temperature 75—150° and the same time.

2-Bromothiophene is less reactive than thiophene, and in comparable conditions it gives a smaller yield of alkyl derivatives [229].

On treating thiophene and its alkyl substituted derivatives with α-pinene or dipentene in the presence of compounds of boron fluoride with water or ethyl ether, viscous oils or resinous products are obtained [233].

Thiophene is alkylated by halogenated olefines in the presence of the catalyst $BF_3 . O(C_2H_5)_2$ at temperatures from —20° to 175° [234]. With allyl bromide 2-(2-bromo*iso*propyl)-thiophene is obtained; with methallyl chloride $CH_2 = C(CH_3)CH_2Cl$ 2-(2-chloro-*tert.*-butyl)-thiophene and small amounts of the di-substituted derivative are formed [229, 234]; thiophene and $ClCH_2C(CH_3) = CHCl$ in the presence of $BF_3 . O(C_2H_5)_2$ give 1,3-dichloro-2-methyl-2-(2-thionyl)-propane.

Dihydrofuran and dihydropyran condense with various acetals in the presence of $BF_3 . O(C_2H_5)_2$ [235]. Dihydrofuran and $CH_3CH(OC_2H_5)_2$ give 2-ethoxy-3-(2-ethoxypropyl)-tetrahydrofuran. Dihydropyran with $CH_3CH(OCH_3)_2$ and $BF_3 . O(C_2H_5)_2$ forms 2-methoxy-3-(2-methoxypropyl)-tetrahydropyran. Many other acetals react in the same way with dihydropyran [235].

13. ALKYLATION OF ACETOACETIC ESTER

Esters containing active α-hydrogen atoms can be alkylated by alkyl halides, alcohols and ethers in the presence of the catalyst boron fluoride and its compounds.

When acetoacetic ester (0·2 mole) reacts with benzyl chloride (0·1 mole) for 8 hr at room temperature in the presence of BF_3 (0·35 mole) it gives α-benzylacetoacetic ester with a yield of 23 per cent of the theoretical [236]. A mixture of acetoacetic ester and *iso*propyl alcohol saturated with BF_3 and left to react forms α-*iso*propylacetoacetic ester in 40 per cent yield [237]. Even such compounds as ethers, which do not have sufficient activity to react as an acceptor of electrons with catalysts of basic character, alkylate acetoacetic ester in the presence of BF_3. Thus, on saturating a mixture of acetoacetic ester and di*iso*propyl ether with boron fluoride, α-*iso*propylacetoacetic ester is formed in a yield of 71 per cent. This product is obtained in 41 per cent yield by reacting acetoacetic ester with *iso*propyl acetate [238].

Similarly, acetoacetic ester is alkylated by tertiary butyl alcohol or ether in the presence of BF_3 [239]. On saturating equimolecular quantities of acetoacetic ester and tertiary butyl alcohol with boron fluoride at 0° and allowing the mixture to stand for 6 hr at room temperature, an alkylated β-ketoester is obtained in a yield of 14 per cent. This reaction is of particular interest because it is known with what difficulties tertiary alkyl groups are introduced into active methylene compounds by the usual methods. No less interesting is the fact that in the given reaction, besides the butylation of the methylene group, an interchange also occurs with the alkoxyl groups with the formation of *tert.*-butyl α-*tert.*-butyl acetoacetate.

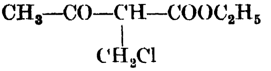
Hauser and collaborators [240, 241] studied in detail the influence of time and temperature of heating on the yield of alkylated acetoacetic ester in the reactions described and found that if acetoacetic ester and *iso*propyl alcohol saturated with BF_3 at 0° were left to stand at 28° for 2—2·5 hr, the yield of ethyl-α-*iso*propylacetoacetate could be increased from 41 to 67 per cent [238]. A mixture of acetoacetic ester and *iso*propyl ether in the presence of BF_3, left for 12 hr at a temperature of 33°, forms α-*iso*propylacetoacetic ester in 61 per cent yield, on standing for 17 hr it is reduced to 30 per cent, and on standing for 2·5 hr at 29° the product is obtained in 50 per cent yield. Ethyl *tert.*-butyl ether, and also *tert.*-butyl alcohol, on reacting with acetoacetic ester in the presence of BF_3 forms *tert.*-butyl-*a*-*tert.*-butyl acetoacetate with a yield of 6—14 per cent and small amounts of unsaturated polymeric products. *cyclo*-Hexanol with acetoacetic ester and BF_3, left for 1—2 hr at 30°, form ethyl-*a*-*cyclo*hexylacetoacetate with a yield of 32—34 per cent.

Attempts to benzylate acetoacetic ester with *n*-propylbenzyl ether in the usual conditions did not give a positive result [157]. Acetoacetic ester and dibenzyl ether, saturated at a temperature of —70° with boron fluoride and left for 30 min at a temperature of —10°, form ethyl-*a*-benzylacetoacetate in 18 per cent yield.

Acetoacetic ester is not alkylated in the described conditions by *n*-butyl, *sec.*-butyl and *iso*butyl alcohols, ethyl and *n*-propyl ethers [240]. Ethyl-*a*-methylacetoacetate is alkylated by *iso*propyl ether in the presence of BF_3 if the mixture is allowed to stand for 14 hr at 24° with the formation of ethyl-*a*-methyl-*a*-*iso*propylacetoacetate in 55 per cent yield. Ethyl *a*-*iso*propylacetoacetate is not alkylated by *iso*propyl ether in the same conditions, nor is ethyl benzoyl acetate $C_6H_5—CO—CH_2COOC_2H_5$ alkylated in the specified conditions by *iso*propyl alcohol and ether, nor ethyl malonate by *iso*propyl ether and *tert.*-butyl alcohol, in spite of the fact that these esters contain the same methylene group as acetoacetic ester. Nitromalonic esters of the formula $ROOC\text{-}CH(NO_2)\text{-}COOR$ are alkylated by alcohols in the presence of BF_3 [242]. From these data it follows that the alkylation of *β*-ketoesters depends on the reactive capacity of both components (the alkylated and the alkylating). *sec.*-and *tert.*-Alcohols or ethers, and also benzyl ether are capable of alkylating acetoacetic ester in the presence of BF_3, whereas aliphatic primary alcohols or ethers do not alkylate the same *β*-ketoester in similar conditions. Sodiomalonic and sodioacetoacetic esters are fairly easily ethylated by triethyloxonium borofluoride $[(C_2H_5)_3O]BF_4$ in ethyl alcohol with the formation of ethyl derivatives in a yield corresponding to 35 and 47 per cent [243].

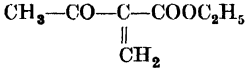
It may thus be considered that the method of Hauser [240] for the preparation of ethyl-*a*-*iso*propylacetoacetate and ethyl-*a*-*cyclo*hexylacetoacetate considerably surpasses the common method for the alkylation of acetoacetic ester through its Na-derivatives. The catalytic method using BF_3 in these conditions is simpler and enables alkyl derivatives to be obtained in higher yield.

Acetoacetic ester and chlorodimethyl ether, saturated with BF_3 at 0°, form methylenediacetoacetic ester with a yield of 33 per cent of the theoretical [244]. It is assumed that the acetoacetic ester is first chloromethylated with the formation of an intermediate C-alkyl derivative (I), which then either alkylates another molecule of acetoacetic ester and is converted into methylenediacetoacetic ester (III) or loses hydrogen chloride giving α-methylenacetoacetic ester (II), and enters into reaction with another molecule of acetoacetic ester forming the same final product (III):



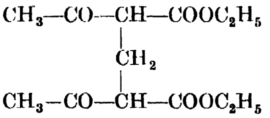
$$CH_3{-}CO{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}{-}COOC_2H_5$$

(I)



$$CH_3{-}CO{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}{-}COOC_2H_5$$

(II)



$$\begin{array}{l} CH_3{-}CO{-}CH{-}COOC_2H_5 \\ \qquad\qquad\quad | \\ \qquad\qquad\; CH_2 \\ \qquad\qquad\quad | \\ CH_3{-}CO{-}CH{-}COOC_2H_5 \end{array}$$

(III)

14. ALKYLATION OF AMINES

Aliphatic aromatic amines and aniline are not alkylated by olefines in the presence of BF_3, because the latter readily combines with such amines to form stable coordination compounds and is deactivated. Amines possessing weaker basic properties, for example, diphenylamine, are alkylated by di*iso*butylene in the presence of $BF_3 . 2H_2O$.

Alcohols in large excess may alkylate aniline at the expense of the active hydrogen atoms of the amino group in the presence of BF_3 [245]. If 2 moles of aniline and 10 moles of ethyl alcohol are heated for 20 hr at 215° with 2 moles BF_3, ethylaniline is formed in 15 per cent yield and diethylaniline in 75 per cent yield. If 3 moles aniline, 13 moles ethyl alcohol and 0·75 mole BF_3 are taken for the reaction and the mixture is heated at 180° for 17 hr, ethylaniline is obtained in a yield of 69 per cent of the theoretical.

Some esters of carboxylic acids are alkylated by *tert.*-aliphatic aromatic amines in the presence of $BF_3 . O(C_2H_5)_2$. The ethyl ester of methane tricarboxylic acid $HC(COOC_2H_5)_3$ and dimethylbenzylamine with $BF_3 . O(C_2H_5)_2$ on heating to 190° for 19 hr form β-phenylpropionic and dibenzylacetic acids as well as other products [246.]

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CHAPTER VI

BORON FLUORIDE COMPOUNDS IN POLYMERIZATION REACTIONS

IN 1873 the polymerization of *iso*butylene in the presence of boron fluoride was discovered by A. M. Butlerov and V. Goryainov [1, 2]; however, until the 1930's this catalyst did not attract any attention, if the individual observations [3—6] are not counted.

Up to 1936 only a few papers were devoted to the part played by halogenated boron compounds (especially BF_3) as catalysts for polymerization [7]. During 1936, however, the catalytic action of halogen compounds of boron in polymerization processes is considered in sixteen papers.

In recent years the use of boron fluoride as a catalyst for polymerization has grown rapidly, and by 1953 the number of investigations and patent claims for the use of BF_3 for the polymerization of unsaturated compounds was about 400.

Boron fluoride is used for the polymerization of unsaturated hydrocarbons and various reactive compounds including oxygen, sulphur, nitrogen, silicon and other elements independently or as coordination compounds with water, mineral acids and organic compounds containing oxygen. Moreover, technically important products are obtained. The degree of polymerization of unsaturated compounds depends on the structure of the polymerizing compound, on the temperature, pressure, time of contact, solvent used and on the character of the boron fluoride coordination compound.

According to the results of A. V. Topchiev and Ya. M. Paushkin [8, 9] catalysts for the polymerization of unsaturated hydrocarbons at a temperature from 20 to 100° are arranged in order of decreasing activity as follows:

$$BF_3 . H_3PO_4 > H_4P_2O_7 . 2BF_3 > BF_3 . HPO_3 > BF_3 . H_2O > AlCl_3 > HF > BF_3 . 2\tfrac{1}{2}H_2SO_4 > BF_3 . ROH > BF_3 . RCOOH > BF_3 > BF_3 . O(C_2H_5)_2 > BF_3 . RCOOR > H_3PO_4$$

The different activity of catalysts based on boron fluoride allows the degree of polymerization to be controlled to some extent, and polymers which are different in outward appearance and in properties to be obtained from the same unsaturated compounds.

1. POLYMERIZATION OF OLEFINES

The lower olefines, ethylene, propylene and *n*-butylenes, are not polymerized at atmospheric pressure in the presence of boron fluoride ethyl etherate [10]. Ethylene is particularly stable to polymerization. A. M. Butlerov showed that ethylene does not undergo polymerization with BF_3 in a sealed tube on heating to 200°. Later, Gasselin [4, 11] confirmed A. M. Butlerov's results and found that with water ethylene is converted in the presence of boron fluoride into boron fluoride ethyl etherate, and not into ethylene fluoroboric acid $C_2H_4 . H_2BO_2F$ or ethoxyfluoroboric acid $C_2H_5OB(OH)F$, as Landolph [12—14] and other investigators [15] considered probable.

At increased pressure ethylene in the presence of boron fluoride and its coordination compounds is polymerized into oily products possessing high viscosity and good lubricating properties [16—23]. The most satisfactory conditions for the polymerization of ethylene into oily products are room temperature and a 10 : 1 molar ratio of ethylene to boron fluoride. In the polymerization of, for example, 100 g ethylene in the presence of 10 g BF_3 under a pressure of 110 atm for 8 hr, a polymer is obtained with the following yield:

Temperature (°C)	Yield of polymer (g)	Viscosity, (P)
0	10	7·156
15—20	85—96	0·759
100	37	0·350
200	60	0·138
300	73	—

As is evident, at room temperature ethylene is polymerized almost completely with BF_3. With increase of temperature the viscosity of the polymer is reduced.

The presence of small quantities of water accelerates the polymerization [24], and not only in the given case: the rate of polymerization of all olefines in general increases considerably when BF_3 is used with a small quantity of water or hydrofluoric acid [16, 22, 25, 26]. The part played by the addition of HF to BF_3 in polymerization evidently consists in the formation of the strong fluoroboric acid HBF_4, which is known only in aqueous solutions [10].

Finely dispersed nickel powder with boron fluoride accelerates the process of polymerization and improves the quality of the oil [27]. For example, in comparable conditions the polymerization of ethylene with

BF_3 only proceeds to 20 per cent, but in the presence of BF_3 and fine nickel powder, to 100 per cent. The oil obtained in the latter case is more transparent and less viscous than without nickel powder. However, the addition of nickel to boron fluoride, although it accelerates the polymerization, decreases the extent of it and gives a less viscous oil, as is seen from the data of Table 64 [10].

Table 64. *Influence of the introduction of* Ni *to* BF_3 *on the polymerization of ethylene**

Boiling range of polymer (°C/mm)	Composition of oil (vol. %)	
	Catalyst BF_3	Catalyst BF_3+Ni
Up to 100/15	0·5	20
Up to 150/15	8·0	45
Up to 150/3	18·0	62
Up to 200/3	40·0	84

*In the first case the viscosity of the oil (at 20°) amounts to 2·17 P, and in the second to 0·68 P.

The crude oils obtained by the polymerization of ethylene have a reddish-brown colour, contain 5—5·5 per cent BF_3 and therefore fume in air. By heating them, boron fluoride can be regenerated quantitatively. Elementary analysis of the oil leads to the formula $(CH_2)_n$. According to the relationship of viscosity to temperature these oils do not comply with standard oils, as is seen from Table 65.

Table 65. *Viscosity of oils in relation to temperature*

Oil	Catalyst	Viscosity (P)		
		20°	50°	95°
Synthetic oil	BF_3 + Ni	0·66	0·147	0·037
Synthetic oil	BF_3	2·17	0·320	0·065
Synthetic oil	BF_3	3·93	0·483	0·090
Spindle oil (Amer.)	—	0·53	0·483	0·038
Refined (Amer).	—	2·18	0·328	0·089
Compressor (Amer.)	—	3·84	0·483	0·095

Pressure exerts a large influence on the degree of polymerization of ethylene in the presence of BF_3. Thus, from 100 g ethylene in the presence of 10 g BF_3 for 14 hr at a pressure of 70 atm 25 g of oil is obtained, and at 130 atm 85—95 g.

The polymerization products of ethylene, obtained with the catalyst BF_3 in the presence of Ni powder and a small amount of water at 20—25°, 50 atm pressure and a reaction time of 150 hr, distil at atmospheric pressure up to 200° 12 per cent, up to 250° 33 per cent and up to 300° 65 per cent [28]. The bromine value of the fraction boiling up to 200° is about 100; of the fraction 200—250° about 70—80 and of the fraction 250—300° about 60. These results show that the polymer consists mainly of olefinic hydrocarbons.

By varying the conditions and selecting the corresponding additions to BF_3, the polymerization of ethylene may be directed in such a way that the main products obtained will be not oils but liquid hydrocarbons boiling in the range corresponding to benzine [29—31]. For example, if 15 g KHF_2 and 74 g BF_3 are put into an 850 ml rotating autoclave and 143 g ethylene is passed in over 4 hr, a polymer is obtained which on distillation gives 3 · 4 per cent by wt. of a fraction boiling up to 20°, and 23 · 9 per cent by wt. of a fraction boiling in the range 20—207° [29]. The polymerization of ethylene in the presence of BF_3 and HSO_3F also gives products which contain 50 per cent by vol. of hydrocarbons boiling in the range corresponding to benzine and having a saturated character and high octane number [32]. By passing liquid ethylene and BF_3 rapidly at a temperature of 8—10° and 50 atm pressure over nickel powder, α-butylene is formed in considerable quantities [33].

A. V. Topchiev and Ya. M. Paushkin [10] showed that ethylene in the presence of the catalyst $H_2O + P_2O_5 + BF_3$ is polymerized even at atmospheric pressure, but the reaction proceeds very slowly: when 10 l. ethyllene were passed through the reaction column at a temperature of 100° and atmospheric pressure several ml of polymer were collected.*

In contrast to ethylene, propylene in the presence of BF_3 and its coordination compounds is polymerized even at atmospheric pressure [34, 35]. In practice, however, the polymerization of propylene is carried out under a pressure sufficient to keep it the liquid state. Moreover, depending on the conditions liquid polymers of the motor fuel type, oily or resinous high-molecular compounds, are obtained [22, 25, 30, 31, 36—45].

Table 66. *Influence of* H_2O *and* HF *on the polymerization of propylene with* BF_3

Catalyst	Time of reaction (hr)	Yield of polymer (% of theoretical)
BF_3	15	30
BF_3 (3 g) + H_2O (1 g)*	15	75
BF_3 (3 g) + HF (1 g)	0·5	100

*Moist propylene taken.

Eighty years ago A. M. Butlerov and V. Goryainov [1, 2] first found that under the influence of BF_3 in a sealed tube at room temperature propylene undergoes thorough polymerization with the formation of oily products of high molecular weight with the complete absence of dimers and trimers. During the second world war products of this type found practical use as synthetic oils [46].

Propylene is polymerized particularly readily in the presence of the catalyst BF_3 and of activators such as HF and organic compounds containing oxygen. The data of Table 66 [10] give some idea of the influence of additions of water and hydrofluoric acid on the rate of polymerization of propylene.

A. V. Topchiev and Ya. M. Paushkin [9, 10, 47—49] studied the polymerization of propylene and butylenes in the presence of different coordination compounds of boron fluoride and found that the boron fluoride coordination compound with metaphosphoric acid was the most active polymerization catalyst for propylene. In the presence of this catalyst, applied on active carbon, propylene is easily polymerized at atmospheric pressure and a temperature of 100°. The polymerization proceeds still more vigorously under pressure, which prevents substantial losses of BF_3 which is easily split off from the metaphosphoric acid at 100—150°. With this catalyst the polymerization proceeds more thoroughly than with $BF_3 . H_3PO_4$ and products are obtained with higher boiling point and greater specific gravity [47].

Oily polymers of propylene are also obtained by the polymerization of propylene in the presence of 0 · 1—25 mole per cent BF_3 and 0 · 05—5 mole per cent of the promoter, iron silicate [50], or BF_3 and sulphur dioxide [51]. Oils obtained by the polymerization of propylene with BF_3 under pressure have a high viscosity, start to boil at 120° (15 mm) and are 50 per cent distilled up to 300°.

When α- and β-butylenes are heated on a boiling water bath with unsubstituted carboxylic acids in the presence of boron fluoride ethyl etherate, the butyl esters of the corresponding acids are formed with a good yield, but the butylenes do not undergo any noticeable polymerization [52]. Pseudobutylene is particularly resistant to polymerization.

In the presence of the catalyst $BF_3 + HPO_3$ *n*-butylenes are polymerized to products boiling in the range 40—350° and containing olefine [47]. In many patents [40, 42, 53—55] it is recommended that for the polymerization of *n*-butylenes into unsaturated liquid or high-molecular viscous products the catalyst BF_3 or its hydrates be used.

The higher *n*-olefines, amylenes, hexylenes, etc., in the presence of boron fluoride and its coordination compounds polymerize more easily. The polymers formed have a molecular weight 2000—5000 and are generally used as lubricating oils.

Iso-olefines polymerize very vigorously in the presence of BF_3 and its coordination compounds. During the last 15 years *iso*butylene has aroused the most general interest among research workers engaged in polymerization. In the whole of organic chemistry it is difficult to find another compound which would constantly attract the attention of research workers. Taking as an example the polymerization of this hydrocarbon in the presence of sulphuric acid, A. M. Butlerov [2] studied the mechanism of the polymerization of olefines. Subsequently the most varied catalysts have been used for the polymerization of *iso*butylene.

In the presence of BF_3 and its coordination compounds *iso*butylene may be polymerized both in the gaseous and in the liquid phases, independently and in admixture with other unsaturated compounds, in the temperature range from -110 to $+250°$. Moreover, depending on the polymerization conditions and the boron fluoride coordination compound taken, low-molecular compounds (dimers and trimers) which are transparent readily volatile liquids, syrupy liquids or viscous oils, elastic rubber-like products or solid polymers with a molecular weight of about 500,000, are obtained.

The polymerization products of *iso*butylene have already been put on the market for over 10 years under the names of Korozil, Oppanol B, Vistanex, Anzolin, etc., and are recommended as rubber substitutes, ingredients of rubber mixtures, plasticizers, substances which increase water resistance, and lubricating oil additives [56—58].

Boron fluoride has an extraordinarily high catalytic activity in regard to *iso*butylene. For the polymerization of *iso*butylene it is sufficient to take BF_3 in a quantity of 0 · 03—0 · 1 per cent. In all, the reaction lasts only a fraction of a second and proceeds very vigorously with the evolution of heat and without any visible decrease of rate with reduction of temperature. Data about the polymerizing activity of BF_3 in comparison with some other catalysts are given in Table 67 [59].

Table 67. *Catalytic activity of catalysts in the polymerization of* iso*butylene at* — 78° [59]

Catalyst		Time of reaction	Yield of polymer (%)	Mol. wt. $\times 10\text{m}^3$
Formula	%			
BF_3	0·05	seconds	100	120—150
$AlBr_3$	0·05	1— 5 min	70—90	120—150
$TiCl_4$	0·12 0·25	20—70 min	35—50	100—130
$TiBr_4$	1·0—1·5	12—58 hr	30—50	70—90
BCl_3	0·9—1·5	12—58 hr	0·5—1·5	30—50
BBr_3	0·6—1·0	12—58 hr	0·5—1·5	20—30
$SnCl_4$	1·5—2·5	17—50 hr	10—18	12—25

Boron fluoride coordination compounds show different catalytic activity in the high-molecular polymerization of *iso*butylene and enable products of different degrees of polymerization to be obtained [60].

The presence of solvents such as toluene and heptane generally decreases the degree of polymerization and gives polymers of low molecular weight.

The temperature and purity of the *iso*butylene exert a substantial influence on the degree of polymerization of *iso*butylene in the presence of BF_3. Usually the molecular weight of poly*iso*butylene increases linearly with decrease of temperature of polymerization. For example, at a temperature of — 10° a poly*iso*butylene is obtained with a molecular weight equal to 10,000, at — 80° about 70,000 and at a temperature of — 103° a poly*iso*butylene may be obtained with a molecular weight of 200,000 [61]. The molecular weight in its turn influences the outward appearance and properties of poly*iso*butylene, as is clearly seen from Table 68 [62].

Table 68.

Approx. mol. wt.	Character of product
1 500	Viscous liquid
10,000	Very viscous semi-liquid mass
100,000	Elastic hard mass
200,000	Elastic hard mass

Poly*iso*butylene with a molecular weight higher than 15,000 is obtained only by polymerizing very pure *iso*butylene [63]. The presence of the most insignificant amounts of other olefines (except ethylene and propylene) in the *iso*butylene decreases the degree of polymerization, and the *iso*butylene polymers formed have a lower molecular weight [64—68]. *iso*Butylene which contains considerable quantities of normal butylenes gives poly*iso*butylene with a large tri*iso*butylene content. When *iso*butylene with different quantities of *n*-butylenes is polymerized in the presence of BF_3 at a temperature of — 95° polymers are obtained with lower molecular weight the more *n*-butylenes there are in the *iso*butylene, as is seen from the following data [61]:

n-Butylenes (%)	Mol. wt.	*n*-Butylenes (%)	Mol. wt.
0	225,000	10	80,000
2	200,000	20	55,000

The presence in the *iso*butylene of even insignificant amounts of dimers and trimers of *iso*butylene greatly retards the polymerization of the *iso*butylene, decreases the yield and molecular weight of the poly*iso*butylenes and leads to the formation not of rubber-like, but of oily polymers [65].

The lower paraffins and olefines (ethylene and propylene) and substances such as methyl chloride do not exert any harmful influence on the polymerization of *iso*butylene in the presence of BF_3, and therefore they are generally used as readily volatile diluents which have the property of maintaining an even temperature. Ethylene, ethane, propane and butanes are used particularly frequently for this purpose [51, 69—74]. The presence of hydrogen sulphide and mercaptans decreases the rate of polymerization of *iso*butylene in the presence of BF_3 and leads to the formation of less complex polymers [69, 74]. Ammonia deactivates the catalyst [51, 59]. Hydrogen chloride, which usually promotes low-molecular polymerization, in this case has the property of forming poly*iso*butylenes of lower molecular weight [60].

However, as was found by many investigators [75—87], absolutely pure *iso*butylene in the presence of BF_3 at a temperature of —80° does not undergo polymerization. In order to start the polymerization the presence of even a trace of a third substance is necessary. This third substance may be water, monohydric alcohols, organic carboxylic acids, phenols and in part ethyl ether and acetone.

Low-molecular Polymers of iso*Butylene*

Low-molecular polymers of *iso*butylene, the dimers and trimers, are formed in the polymerization of *iso*butylene in the gaseous phase in the presence of 0 · 1—1 · 0 per cent BF_3 at a temperature of 100—150° and an exposure of less than 1 sec, and the subsequent rapid treatment of the reaction products with water vapour or the introduction into the reaction, for a few seconds after the beginning, of agents which weaken the polymerization [88—93]. If a stream of BF_3 is passed through the boiling *iso*butylene, polymers are produced which take the form of a transparent oily liquid having a molecular weight of 220 and 50 per cent of which boil up to 250° [62].

For the polymerization of *iso*butylene into the low molecular hydrocarbons, di*iso*butylene and tri*iso*butylene, boron fluoride ethyl etherate [94, 95] and other coordination compounds may be used as catalysts. In 1936—1938 S. V. Zavgorodnii [52] found that *iso*butylene in the presence of carboxylic acids and $BF_3 . O(C_2H_5)_2$ at a temperature of 50° or higher is immediately polymerized into oily products.

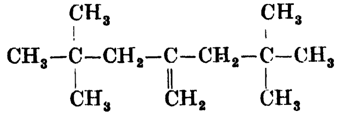
The low-molecular polymerization of *iso*butylene in the presence of BF_3 and its coordination compounds was studied in detail by A. V. Topchiev and his collaborators [96—98]. It was found that over the complex $Na_2SO_4 . 2BF_3$ *iso*butylene polymerizes only at increased temperature at the moment of dissociation of the complex with the formation of free boron fluoride [98]. In the presence of 1—2 per cent boron fluoride ethyl etherate the polymerization of *iso*butylene proceeds vigorously in the liquid phase at a temperature of 20° and 4 atm pressure, and in the gaseous phase by passing *iso*butylene through a column filled with activated carbon moistened with $BF_3 . O(C_2H_5)_2$ at a temperature of 10—130° and atmospheric pressure. The polymerization proceeds almost quantitatively (90—95 per cent). The polymer obtained by the gas-phase and by the liquid-phase polymerization does not differ substantially in composition and boils in the range 30—220°. On distillation there is obtained on an average 20 per cent of a fraction with b.p. 100—110°, corresponding to the dimer of *iso*butylene, 70 per cent of a fraction with b.p. 160—180°, corresponding to the trimer of *iso*butylene, and 10 per cent residue. Sp. gr. of polymeric benzine d_4^{20} 0 · 750; octane number 92.

Temperatures within the range 10—130° and the surface of the carrier of the catalyst do not affect the total yield of polymer and the ratio of the separate fractions. However, it is expedient to carry out the gas phase polymerization at a temperature of 5° in order to hold the catalyst better on the bearer.

Detailed study of the polymerization products showed that in fact the dimers and trimers are not formed in the quantities assumed on the basis of the fractional composition quoted, because the bromine values of the polymers (30—36) are very low for pure dimers (143) and trimers (93). It is therefore considered probable that during the polymerization, cyclization and dehydrogenation take place leading to the formation of naphthenes and other hydrocarbons.

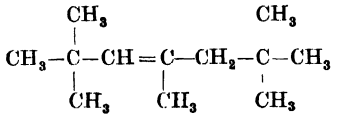
In the polymerization of *iso*butylene in the liquid phase in the presence of the catalyst $BF_3 . H_3PO_4$ at a temperature of —10°, from 50 ml hydrocarbon 12 ml of polymer is obtained in the form of an oily transparent liquid of sp. gr. d_4^{20} 0 · 817, 50 per cent of which boils within the range 90—250°. The residue, which boils above 300° and constitutes about 20 per cent of the volume, has d_4^{20} 0 · 859 [9, 48, 49].

The structure of the dimers [97] and trimers [99] of *iso*butylene, obtained with the catalyst $BF_3 . O(C_2H_5)_2$, has been studied; from the oxidation products it was found that the trimer of *iso*butylene consists of the isomers (I) and (II), and probably contains small amounts of the isomers (III) and (IV), i.e. it is similar to the tri*iso*butylene of A. M. Butlerov:



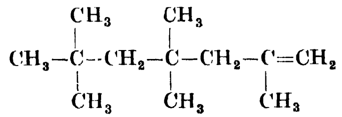
$CH_3-C(CH_3)_2-CH_2-C(=CH_2)-CH_2-C(CH_3)_2-CH_3$

(I)



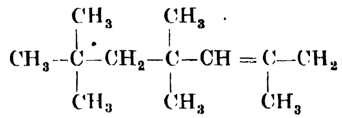
$CH_3-C(CH_3)_2-CH=C(CH_3)-CH_2-C(CH_3)_2-CH_3$

(II)



$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-CH_2-C(CH_3)=CH_2$

(III)



$CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-CH=C(CH_3)-CH_2$

(IV)

*Poly*iso*butylenes of molecular weight 10,000—20,000.*

*iso*Butylene, carefully purified from impurities which lower the degree of polymerization, forms polymers of molecular weight 10,000—20,000 in the presence of BF_3 in easily volatile diluents (for example, ethylene, ethane, propane, butane) or in inert solvents (CCl_4, heptane, benzene and toluene) at a temperature of about $-10°$ [100—116]. In the case of *iso*butylene containing *n*-olefines, the polymerization is carried out at lower temperatures, for example at $-80°$.

Poly*iso*butylenes of medium molecular weight constitute a viscous or semi-solid viscid mass; they are used as additives which improve the viscosity-temperature characteristics of oils, and as plasticizers.

Higher Polymers of iso*Butylene*

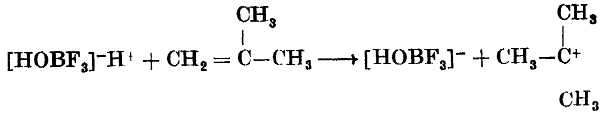
Poly*iso*butylenes of molecular weight 100,000—500,000 are obtained by the polymerization of *iso*butylene with BF_3 in easily volatile diluents (more frequently in ethylene) at a temperature from -80 to $-150°$ [117—130]. These are the elastic solid products which may be formed, and in their physical properties they are near to rubbers. In resistance to corrosion poly*iso*butylenes of the molecular weight indicated surpass all other known materials of this type [62], resist the action of oxidizing agents, possess high resistance to water, swell and dissolve like rubbers, but do not display any elastic recoil at ordinary temperatures. They are used for the preparation of adhesive and sealing compounds, as insulating materials, for the manufacture of acid-resistant linings and other purposes. Poly*iso*butylenes of lower molecular weight are used as additives for increasing the index of viscosity of mineral oils [131, 132].

Essential defects of rubber-like poly*iso*butylenes are their high saturation and as a result of this their incapacity of being vulcanized. It is therefore recommended that poly*iso*butylenes of high molecular weight be halogenated by the action of halides in the presence of BF_3 in solvents (carbon tetrachloride) at a temperature of 32—175° [133, 134]. As a result of splitting off hydrohalic acids, unsaturated poly*iso*butylenes capable of being vulcanized are obtained.

The special interest shown recently in the polymerization of *iso*butylene in the presence of boron fluoride is explained first by the wide possibilities of preparing a variety of valuable products, and secondly by the range of the specific features of the reaction. Low-temperature polymerization of *iso*butylene with BF_3 proceeds almost with explosive violence [65]. However, the polymerization of *iso*butylene cannot be started if the concentration of boron fluoride does not exceed a certain limit [76]. In some conditions *iso*butylene does not polymerize if BF_3 added is to the hydrocarbon slowly. Sometimes *iso*butylene does not completely polymerize in a mixture with boron fluoride (in the absence of even traces of H_2O). It follows from this that boron fluoride as such is probably not the catalyst which initiates the polymerization reaction, and it is impossible to explain the peculiarities of this reaction by a simple kinetic scheme.

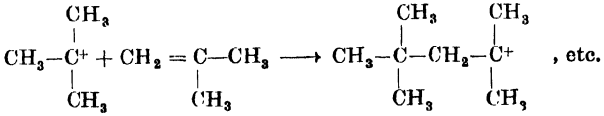
We consider it probable that the first stage of the polymerization is the reaction of BF_3 with substances which are present even as impurities, such as H_2O, ROH and others which form complexes which initiate the polymerization. If, for example, water is present in the *iso*butylene, the boron fluoride forms a complex with the water, the monohydrate (I). Next, the boron fluoride monohydrate, having an active proton, attacks the *iso*butylene and forms the carbonium ion (II). The latter then initiates the chain polymerization with the formation of polymers in which the monomeric molecules are combined in a "head to tail" manner. The mechanism may be represented by the following scheme :

$$BF_3 + H_2O \longrightarrow \underset{(I)}{BF_3 \cdot H_2O} \rightleftharpoons [HOBF_3]^{-}H^{+}$$



$$[HOBF_3]^-H^+ + CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3 \longrightarrow [HOBF_3]^- + CH_3-\underset{CH_3}{\overset{\overset{CH_3}{|}}{C^+}}$$

(II)

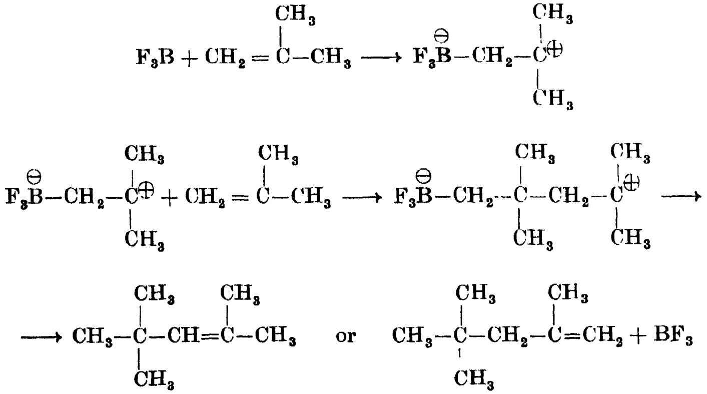


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} + CH_2=\underset{\underset{CH_3}{|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}\quad\text{, etc.}$$

(III)

The reaction is completed by the interaction of the anion $[HOBF_3]^-$ with a polymeric carbonium ion when no monomeric molecules of *iso*butylene remain in the mixture.

The mechanism stated is not absolutely general for the polymerization of all olefines. It is possible that the low-molecular polymerization of *iso*butylene with BF_3 proceeds through the stage of the formation by the monomer and the catalyst of a complex catalyst-carbonium ion which then initiates the reaction according to the scheme [99]:



$$F_3B + CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3 \longrightarrow F_3\overset{\ominus}{B}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\oplus}}}$$

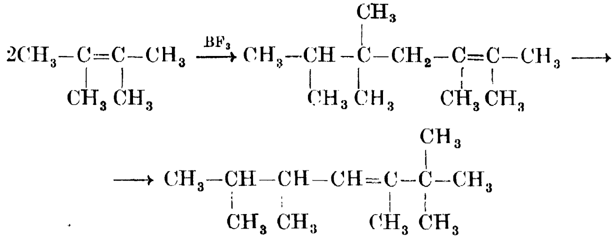
$$F_3\overset{\ominus}{B}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\oplus}}} + CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3 \longrightarrow F_3\overset{\ominus}{B}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\oplus}}} \longrightarrow$$

$$\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 \quad\text{or}\quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2 + BF_3$$

The easily initiated polymerization of styrene is also brought about by means of a bimolecular reaction between the monomer and a complex of the catalyst with the monomer, i. e. by the formation of a complex catalyst-carbonium ion which starts the chain reaction [135].

Other iso-olefines, for example *iso*amylene, are easily polymerized in the presence of BF_3 [136—138]. *iso*Amylene, in the presence of boron fluoride ethyl etherate is polymerized at 10—130° with the formation of polymers (yield in the liquid phase 80 per cent, yield in the gas phase 90 per cent) which consist of 80 per cent decylene boiling in the range 148—156° and having an octane number of 85 [96]. The quantity of catalyst for the liquid phase polymerization in this case amounts to 1—2 per cent, but for the gas phase polymerization, which was carried out with the catalyst applied to activated carbon, it was smaller than this.

Tetramethylethylene, when treated with boron fluoride at a temperature of from 10 to —60°, gives 2,2,3,5,6-pentamethylheptene-3. It is probably formed by the isomerization of the dimer of tetramethylethylene [139];



$$2CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3 \xrightarrow{BF_3} CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3 \longrightarrow$$

$$\longrightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH=\underset{CH_3}{C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

This example shows that the polymerization of olefines with BF_3 proceeds not by the condensation of simple molecules into complex ones, but is accompanied at the same time by the isomerization of the polymers formed or by the partial isomerization of the original olefines before their polymerization.

Absolutely pure di*iso*butylenes, like butylene, are not polymerized in the presence of BF_3. The presence of a third component is necessary to start the reaction [81, 140—142]. Therefore non-purified di*iso*butylene in the vapour state polymerizes fairly quickly with BF_3, but the distillate purified *in vacuo* over metallic sodium is not polymerized with BF_3 at a temperature of 60°. If, however, a small amount of a third component, water or alcohol (in the vapour state) is added to the vapour of di*iso*butylene which has been purified as shown above and mixed with BF_3 the polymerization proceeds very vigorously.

The part played by the third component in this case without doubt consists in the formation with boron fluoride of highly active protonic complexes which start the polymerization, and this may be confirmed by the following facts. When oxygen, H_2S or HCl are added to the purified di*iso*butylene and boron fluoride as a third component, polymerization is not observed (boron fluoride does not form active complexes with the components indicated), but if a little water is introduced into this non-reacting mixture, polymerization invariably begins immediately. The presence of phenol activates the polymerization. Instead of BF_3, boron fluoride ethyl etherate may be used as the catalyst [43]. Polymers of di*iso*butylene and other iso-olefines always have the character of oily products and the formation of rubber-like substances was never noted.

In many patents [144—155] boron fluoride is recommended as a catalyst for the polymerization of the cracking products of petroleum, its fractions (light and heavy) and other mixtures containing considerable amounts of olefines, diolefines and substituted aromatic hydrocarbons. The polymers thereby formed as viscous liquids are used as lubricating oils, and the hard pale-coloured resins are used as additions to lubricating oils or for coats of lacquer.

The halo-olefines 3,3,3-trifluoropropene and 2-methyl-3,3,3-trifluoropropene are capable of being polymerized in the presence of boron fluoride [156].

*Polymerization of cyclo-olefines. cyclo*Pentene and *cyclo*hexene in the presence of BF_3 or $BF_3 + HF$ polymerize to liquid dimers and trimers and higher polymers which are hard transparent resins of amber yellow colour [16, 22, 31, 157].

Acenaphthylene, on treatment with boron fluoride in benzene or chlorobenzene at 0°, is polymerized quantitatively to high-molecular products with a molecular weight of the order of 15,000 [158, 159].

2. POLYMERIZATION OF VINYL- AND ALLYL-DERIVATIVES OF CARBO- AND HETERO-CYCLIC COMPOUNDS

4-Vinyl*cyclo*hexene [160, 161] and styrene [162—165] in the presence of BF_3 or $BF_3 . O(C_2H_5)_2$ in solvents or without solvents, are vigorously polymerized with considerable evolution of heat to viscous oily or solid polymers. If a few drops of $BF_3 . O(C_2H_5)_2$ are added to 5—10 ml styrene at room temperature polymerization begins instantaneously, the mixture boils, and in a few minutes a solid polystyrene is formed which is easily ground to a white powder with a m. p. 160—165°, dissolves well in benzene and does not dissolve appreciably in alcohol and ether. In the presence of 0·8 per cent by weight of BF_3 in ethyl chloride styrene forms a polymer with molecular weight 60,000. 2,6-Dimethyl-4-*tert.*-butylstyrene in CCl_4 with BF_3 is polymerized to a glassy product with m. p. 180—190° [166].

*iso*Propenylbenzene or *a*-methylstyrene [167], *p*-*iso*propenyltoluene [168, 169] and other arylalkenes [170] readily undergo polymerization in the presence of BF_3. *p*-*iso*Propenyltoluene $CH_2 = C(CH_3)C_6H_4CH_3$ (200 parts) treated with $BF_3 . O(C_2H_5)_2$ (1—2 parts) at a temperature of 0° or over gives viscous liquid polymers, the lower fractions of which have good electrical properties and may be used as insulating oils. At a temperature below 0° (from —40 to —80°) granular or powdery polymers are formed with sharply defined crystallinity and high softening point.

Vinyldiphenyl $CH_2{=}CH{-}C_6H_4{-}C_6H_5$ with 5 per cent BF_3 or $BF_3 . O(C_2H_5)_2$ in the solvents toluene, methyl chloride or ethyl chloride at low temperatures (from -10 to $-50°$) polymerizes into high-molecular solid brittle polymers with high softening point [171].

1-Vinylpyrene with $BF_3 . O(C_2H_5)_2$ is quantitatively converted into a polymer with a softening point of about 200° [172]. 2-Vinyldibenzofuran with BF_3 is also polymerized to high-molecular products which possess good electrical properties [173, 174]. N-Vinylpyrrole and N-vinylcarbazole are polymerized with BF_3 in a solution of methylene chloride at a temperature below 20° [175].

Polymerization of Vinyl and Allyl Ethers

A survey of the literature shows that all vinyl ethers (vinylalkyl, vinylacyl, vinylaryl, vinylhydroaryl and vinylheterocyclic) are readily polymerized in the presence of boron fluoride and its coordination compounds. $BF_3 . O(C_2H_5)_2$ and $BF_3 . 2H_2O$ are more often used in practice and the process is carried out at low temperatures.

In recent years much attention has been paid to the polymerization of vinylalkyl ethers in the presence of BF_3 and its coordination compounds. The simple and convenient methods of preparing these ethers, worked out by A. E. Favorskii, M. F. Shostakovskii and their collaborators have no doubt contributed to this [176].

The polymerization is as a rule carried out in solvents. Depending on the ether taken and the reaction conditions polymers of the most varied properties are obtained.

Vinylalkylethers in the presence of BF_3 or $BF_3 . O(C_2H_5)_2$ at low temperatures (from -10 to $-80°$) generally condense to rubberlike products which may be used as insulating materials, components of varnish coatings for wood, paper, leather, for the preparation of glue and so on. At increased temperatures sticky viscous polymers are obtained [101, 177, 178].

Vinylbutyl ether with BF_3 in the solvent propane at a temperature of 45—50° was polymerized in Germany on an industrial scale before the second world war [179]. A polymer called opanol C has been recommended for the preparation of a leucoplast and for the gluing of footwear.

M. F. Shostakovskii and collaborators [180, 181] studied the polymerization of vinyl*iso*butyl and vinyl*iso*amyl ethers with a series of catalysts and found that they could be arranged in the following order of decreasing catalytic activity:

$$BF_3 > FeCl_3 > AlCl_3 > SnCl_2 > SiCl_4 > PCl_3 >$$
$$> ZnCl_2 > Cu_2Cl_2 > Si(OC_2H_5)_2Cl_2$$

Vinylphenyl ether is most easily polymerized in the presence of BF_3 with the formation, at low temperatures of reaction, of hard polymers which have particularly valuable properties, as is seen from the data of Table 69 [182].

Table 69. Polymerization of vinylphenyl ether

Catalyst	Amount (%)	Temperature (°C)	Time (hr)	Yield (%)	External appearance of polymer
$AlCl_3$	1·5	—10	1·5	75	Colourless, almost solid
$FeCl_3$	2·0	+10	20	52	Dark yellow liquid resin
$SiCl_4$	3·0	+10	24	65	Dark brown liquid resin
$SiCl_4$	1·5	—10	32	63	Orange liquid resin
BF_3 (50% solution)	0·01	0 to +5	3	72	Colourless, sticky, viscous
	0·02	—10	3	78	Yellow vitreous

It is remarkable that even thick, viscous, gluey polymers of vinylphenyl ether, obtained with BF_3, on drying form a hard, non-glutinous, thermoplastic film.

The results quoted again confirm the idea which is repeatedly expressed in print that it is probably impossible for the present to predict any more suitable catalyst than BF_3 for low-temperature processes of polymerization.

We give a list of vinyl ethers which have undergone polymerization with BF_3 and its coordination compounds:

Methyl [183—185]
Ethyl [183, 186]
*iso*Propyl [187, 188]
n-Butyl [179, 186, 189, 190]
*iso*Butyl [180, 181, 184]
*iso*Amyl [180, 181]
Abietinol [191—193]
β-Diacetonefructose [194]
Diacetoneglucose [194]
Phenyl [192]
Tetrahydrofurfuryl [195]

Boron fluoride and boron fluoride ethyl etherate are suggested [196] as catalysts for the polymerization of vinyl acetate, methyl α-bromacrylate [197], β-phenylvinylthioacetate $C_6H_5CH=CHSCOCH_3$ [198], 1,2-dimethoxyethylene [199], vinyl allyl ether [200], vinyl bromide [197] and other vinyl derivatives [201—203].

Vinyl ethers of abietinol and hydroabietinol are polymerized with BF_3 or $BF_3 \cdot O(C_2H_5)_2$ on heating to 150—250°. The polymers are used as additives to drying oils and alkyd resins [191—193]. Polymers of vinyl ethers of β-diacetonefructose and β-diacetoneglucose [194] are white resins, easily soluble in organic solvents, and are used for the preparation of films.

Allylbenzene, 4-methoxy- and 4-ethoxy-allylbenzenes, according to Staudinger's results [204], are not polymerized in the presence of boron fluoride. 2-Allyl- and 2-methylallyl-phenyl ethers are polymerized with $BF_3 . O(C_2H_5)_2$ with the formation of thermoplastic polymers [205].

Vinylphenoxyacetylene in the presence of $BF_3 . O(C_2H_5)_2$ forms thermoplastic polymers which have a high softening point and may be rolled and moulded [206].

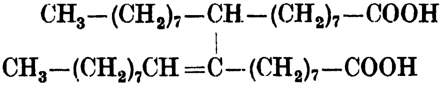
Vinylalkyl ethers are arranged, according to ease of polymerization in the presence of $BF_3 .O(C_2H_5)_2$ at low temperatures, in the following order: vinyl*iso*propyl > vinyl*iso*butyl > vinyl *n*-butyl > vinylethyl > vinylmethyl [207]. Thus, capacity for polymerization is found to be in direct relation to the structure of the alkyl radical. The more branched the chain of carbon atoms of the radical is, the easier is the ether polymerized. This is probably dependent on steric hindrance to the formation of boron fluoride complexes with the oxygen atom of the ethers. Vinylmethyl ether has an unprotected oxygen atom, and therefore BF_3 easily forms with it a strong complex which in some way lowers the chemical reactivity of the double bond, and this ether is polymerized relatively feebly with a small quantity of BF_3 at low temperatures [207]. In vinyl*iso*propyl ether there is great steric hindrance, which protects the oxygen atom. As a result of this, boron fluoride forms a rather unstable complex with this ether, but on the other hand strengthens the chemical reactivity of the double bond, and the ether is very easily polymerized. This inference agrees with the generally known fact that the stability of the boron fluoride complexes with dialkyl ethers decreases in the following order:

$$BF_3 . O(CH_3)_2 > BF_3 . O(C_2H_5)_2 > BF_3 . O(iso\text{-}C_3H_7)_2 \text{ [208]}$$

Polymerization of Unsaturated Acids, their Esters, Mineral, Animal and Vegetable Oils

Undecylic acid, treated with gaseous BF_3 at room temperature, polymerizes to an oily product having an acid character [209]. Chemically pure oleic acid, previously distilled *in vacuo,* does not polymerize in the presence of $BF_3 . O(C_2H_5)_2$ or H_3PO_4. In the presence of 10—20 per cent of the compound of boron fluoride with phosphoric acids, especially orthophosphoric, oleic acid polymerizes almost quantitatively, and the molecular weight of the polymers formed corresponds to dimeric compounds, as found by A. V. Topchiev and T. P. Vishnyakova [210—212].

On the basis of the figures obtained for acid and bromine value, and also of the study of the oxidation products, it was found that the dimer of oleic acid is mainly an unsaturated dicarboxylic acid of the structure:



$$\begin{array}{l} CH_3-(CH_2)_7-CH-(CH_2)_7-COOH \\ \qquad\qquad\qquad\quad\;\; | \\ CH_3-(CH_2)_7CH=C-(CH_2)_7-COOH \end{array}$$

Methyl oleate in the presence of $BF_3 . H_3PO_4$ polymerizes less vigorously. Also, in this case, the products are mainly dimers of the ester [212].

α,β-Unsaturated aliphatic acids and their esters with monohydric and polyhydric alcohols, for example glycols, form insoluble highly fusible resins in the presence of BF_3 by condensation polymerization [213, 214].

Methyl, ethyl and butyl furylacrylates with BF_3, depending on conditions, polymerize to rubber-like products or resins [215].

Methacrylates [216, 217], acrylonitrile [218], acrylamides [219], alkylolamides of acrylic acid [220], glycyl esters of acrylic, methacrylic and crotonic acids [221] in the presence of BF_3 or its coordination compounds easily polymerize to hard or very viscous polymers.

It is recommended that petroleum hydrocarbon oils be treated with boron fluoride with the object of improving their lubricating properties [222—233].

In the presence of BF_3 natural colophony resins (dammar, copal) independently or with phenols and their ethers polymerize to high-quality depressants of lubricating oils [234—239].

Vegetable and animal oils containing esters of unsaturated monocarboxylic acids, for example linseed [240], cotton seed [241], soya bean [242], whale [241], dolphin [243], sperm [244] and other oils [245—247], are converted on polymerization with BF_3 into products which are useful as lubricants, plasticizers and depressants of lubricating oils.

3. POLYMERIZATION OF ACETYLENIC AND DIENIC COMPOUNDS

Acetylene with BF_3 under pressure condenses to rubber-like products having good elastic properties or to liquid polymers of the lubricating oil type [248, 249].

Alkoxyvinylacetylenes [250] react with boron fluoride ethyl etherate with explosive violence and with complete resinification of the substance. A small stick moistened with $BF_3 . O(C_2H_5)_2$ and introduced into the vapour of methyoxyvinylacetylene is instantly covered with a loose, brown polymer. Vinylacetylene and methylallene with SO_2 in the presence of BF_3 at a temperature of 150—250° and increased pressure are converted into high-molecular compounds [251].

Divinyl, *iso*prene, piperylene and other diene hydrocarbons [165, 166, 252—258] in excess of inert diluents in the presence of BF_3 and its coordinations compounds are usually polymerized to high-molecular oily products.

In a number of patents [259—267] it is recommended that rubbers dissolved in CCl_4 or other solvents be treated with boron fluoride with the object of obtaining from them plastics or rubber-like products, but with properties other than the original ones.

Alkoxyprenes $CH_2 = CH\text{-}C(OR) = CH_2$ in benzene solution in the presence of very small amounts of $BF_3 . O(C_2H_5)_2$ are vigorously polymerized to difficultly soluble resins of a brown colour [268]. Formoxy- and acetoxy-prenes are easily polymerized with $BF_3 . O(C_2H_5)_2$ [269]. Halogenated alkoxyprenes with this same catalyst give dark-coloured resins [268].

Cyclic diene hydrocarbons, for example *cyclo*pentadiene, in the presence of boron fluoride are readily polymerized to polycyclenes [270—273].

4. POLYMERIZATION OF TERPENES AND OTHER COMPOUNDS

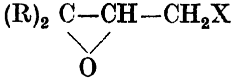
Acyclic and cyclic terpenes (*allo*ocimene, ocimene, myrcene, α- and β-pinenes, dipentene, limonene and squalene) in inert volatile solvents in the presence of BF_3 are polymerized to high-molecular products which are recommended as plasticizers, adhesive compositions and rubber substitutes for many purposes [274—280].

Of the two pinenes the more easily polymerized is β-pinene which gives polymers of higher melting point as seen from the data of Table 70. These results were obtained at identical temperatures and concentrations in the presence of a number of catalysts [276].

Table 70. *Polymerization of pinenes with different catalysts to solid polymers*

Catalyst	α-Pinene		β-Pinene	
	Yield of polymers (%)	m. p. (°C)	Yield of polymers (%)	m. p. (°C)
$AlBr_3$ ...	35·3	85·0	93·2	136
$AlCl_3$	35·2	84·0	94·2	134
$ZrCl_4$	20·0	91·3	96·0	132
$AlCl_3 . O(C_2H_5)_2$	18·0	67·3	76·5	102
BF_3	14·2	67·0	54·0	104
$BF_3 . O(C_2H_5)_2$	11·8	Semi-solid	43·0	68
$SnCl_4$	4·7	—	21·3	—
$BiCl_3$	0·1	—	5·6	—
$SbCl_3$	0·2	—	0·7	—
$ZnCl_2$	0·0	—	0·5	—

Carene with BF_3 in the solvents CCl_4, $CHCl_3$ or chlorethane is polymerized to resins [281]. On heating with BF_3 in a sealed tube at 250° camphor forms polymeric products [282].

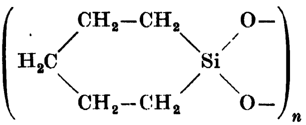
Organic α-oxides of the general formula  $(R)_2\underbrace{C{-}CH}_{O}{-}CH_2X$ are readily polymerized in the presence of BF_3 and its coordination compounds with the formation of liquid or solid polymers [283—287]. Polymers of ethylene oxide obtained with $BF_3 . O(C_2H_5)_2$ are oily liquids which are decomposed on distillation with the evolution of acrolein [283]. Polymers of propylene oxide and epichlorhydrin are viscous oils, but polymers of *cyclo*hexene oxide form a transparent sticky resin. In the case of *iso*butylene oxide it is assumed that at first under the influence of $BF_3 . O(C_2H_5)_2$ it isomerizes to *iso*butyric aldehyde which then polymerizes to resins [283].

Phenoxypropylene oxide [284, 285] and tetramethylethylene oxide [286] with $BF_3 . O(C_2H_5)_2$ may be polymerized both to liquid and to solid polymers, which are used as synthetic lubricants or plasticizers. Ether oxides are capable of being transformed by polymerization in the presence of BF_3 [288]. 1,3-Dioxolanes with aromatic hydrocarbons (alkyl benzenes) [289] or polyhydric alcohols and their derivatives [290] in the presence of BF_3, or BF_3 applied to active carbon, are converted by condensation polymerization and form colourless, viscous liquids with a molecular weight of up to 1800 and are good plasticizers for cellulose. Polymers of 1,2-bismethoxyethane, obtained with BF_3, are used for sizing fabrics or as additions to printing inks [291]. 1,2-Ethoxy-4-(ethoxyethyl)-*cyclo*hexane polymerizes comparatively easily with BF_3 [292].

*iso*Propyl [293] and *tert.*-butyl [294] alcohols with BF_3 at a temperature of 100—160° give polymers of the corresponding olefines. Their formation may evidently be represented in such a way that at first the alcohols split off water and are converted into olefines, and the latter are then polymerized.

Furfural and furfuryl alcohol with BF_3 form low-molecular resins [295].

Cyclic disulphides [296], polysulphides of the general formula $(HOC_nH_{2n})_2S_x$, for example di-(β-hydroxyethyl)-trisulphide [297] and tetraallylsilane [298] polymerize in the presence of BF_3. Silicon compounds of the general formula $R_{4-n}Si(OR')_n$, for example $C_5H_{11}Si(OC_2H_5)_3$, $(CH_3)_2Si(OC_2H_5)_2$ with organic acids in the presence of BF_3 form polyalkylsiloxanes [299] together with esters. Polymers of cyclic organosilicon compounds of the type



may, with BF_3, be converted into more complex polymers [300].

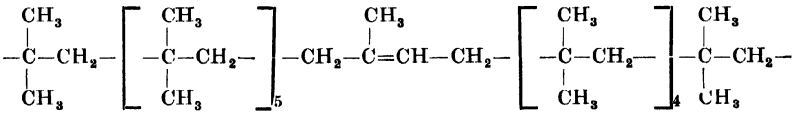
Cyanogen chloride with BF_3 and HCl in a solvent of dioxane or diethyl cellosolve at a temperature of 20—40° is 69—89 per cent converted into chlorocyanuric acid [301]. The nitrile of azelaic acid with formaldehyde in the presence of BF_3 forms polymers of the amide of azelaic acid of composition $(NHCO(CH_2)_7CONHCH_2)_n$ [302].

Boron fluoride together with other catalysts is recommended for the preparation of polymers of alkylmetaphosphoric acid [303—305].

5. COPOLYMERIZATION OF UNSATURATED COMPOUNDS

In the presence of boron fluoride and its coordination compounds with dienic hydrocarbons having conjugate double bonds, the most varied unsaturated aliphatic hydrocarbons may be polymerized together. *iso*Butylene enters particularly easily into copolymerization with such dienes as divinyl, *iso*prene, chloroprene, dimethylbutadiene, pentadiene and dimethylallene [120, 306—320]. BF_3. either free or in the form of etherates, is more often used for copolymerization. The process is carried out at temperatures from 10° to —100° without solvents or better in the liquid diluents: CH_3CHF_2, CH_3Cl, C_2H_4, C_2H_6. Conjugated dienes are used in quantities of 1—20 per cent in relation to the *iso*butylene. The copolymers formed have a molecular weight of from 1000 to 300,000 or more.

A very valuable industrial product is the so-called *butyl rubber* which is a copolymer of *iso*butylene with a small addition of dienic hydrocarbons, mainly divinyl and *iso*prene [61, 62, 177]. Butyl rubber is an elastic, soft, white product, without smell, and with specific gravity 0·91. It contains approximately 100 times fewer double bonds than natural rubber, and is thus an almost saturated high-molecular product [321]. A remarkable property of butyl rubber is its high stability to the action of mineral acids and oxygen, resistance to frost (it does not lose its rubber-like properties at —62°) and non-susceptibility to ageing. In contrast to poly*iso*butylene rubber, butyl rubber vulcanizes, and in structure is a linear polymer:



$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\left[-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\right]_5-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}-\left[-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\right]_4-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-$$

Attemps have been made to bring about the low-temperature emulsion copolymerization of *iso*butylene with divinyl in the presence of BF_3 in inert solvents and perfluoro-hydrocarbons, for example in perfluoro-*m*-xylene and perfluoromethylnaphthalene with perfluoromethyl*cyclo*hexane (1 : 3) [313], but the emulsions formed were rather unstable and the copolymers obtained had poor mechanical properties.

In recent years much attention has been paid to the copolymerization of *iso*butylene and other iso-olefines with styrene at low temperatures (about —100°) [70, 314, 322—327], and also of styrene with butadiene, *iso*prene, dimethylbutadiene and chloroprene [328—333] in the presence of BF_3 or $BF_3 . O(C_2H_5)_2$, as a result of which rubber-like copolymers are formed.

Normal olefines (propylene, *n*-butylenes and others) copolymerize with dienes (butadiene and *iso*prene) in the presence of BF_3 at temperatures below 0° [334—339].

A. V. Topchiev, Ya. M. Paushkin and T. E. Lipatova [60] studied the copolymerization of *iso*butylene with propylene and pseudobutylene in heptane in the presence of BF_3 at a temperature of —80° and found that pseudobutylene, added to *iso*butylene to the extent of 50 per cent, does not lower the molecular weight of the copolymer relative to that of the polymer obtained from *iso*butylene alone. Propylene lowers the molecular weight of the copolymer from 5700 to 1960, as is seen from a comparison of experiments 2 and 3 of Table 71.

Table 71. *Copolymerization of* iso*butylene with pseudobutylene and propylene at* —80°

No. of experiment	Composition of olefines (%)			Catalyst	Mol. wt. of polymer	s. g.	Yield (%)
	iso-C_4H_8	*n*-C_4H_8	C_3H_6				
1	89·4	10·6	0	BF_3	5700	—	96
2	56·7	43·3	0	BF_3	5700	—	91
3	43·4	—	56·6	BF_3	1960	0·823	72
4	47·4	—	52·6	$BF_3 . H_3PO_4$	240	0·810	61
5	76·0	—	24·0	$BF_3 . H_3PO_4$	210	—	—
6	0	—	100	$BF_3 + AlCl_3$	Does not polymerize	—	—

*iso*Butylene and other iso-olefines in the presence of boron fluoride and its coordination compounds copolymerize with the terpenes myrcene, *β*-pinene and dipentene [340, 341], with vinylnaphthalene and indene [324], with acetylene [342] and alkylacetylenes [343], with dialkoxydivinyl, vinyl methacrylate [344], carbomethoxymethylvinyl ether [345] and unsaturated ketones [346].

*iso*Butylene (98 g) and 2,6-dimethyl-4-methylenehexadiene-2,5 (2 g) with BF_3 in ethyl chloride at a temperature of from 0° to —165° form an elastic rubber-like copolymer, approximating in properties to natural rubber [340]. *iso*Butylene and β-pinene with BF_3 in ethyl chloride at —70° give copolymers as low-melting thermoplastic resins or rubber-like products which are capable of being vulcanized [341]. Vinylnaphthalene and indene copolymerize with *iso*butylene with the formation of colourless oils of specific gravity 0·90—0·95 and a viscosity at 210° corresponding to that of lubricating oils [342]. Acetylenic hydrocarbons are converted with *iso*butylene into products with molecular weight about 3000 [343]. *iso*Butylene and diethoxybutadiene (3 per cent) in the presence of BF_3 at a temperature of —101° forms elastomers which are fairly stable to many chemical reagents [347]. *iso*Butylene (18 g) and vinylmethacrylate (2 g) in petroleum ether (60 g) with BF_3 at a temperature of —80° give copolymers with molecular weight 22,000 [345]. *iso*Propenylmethyl ketone, a-methyleneamylmethyl ketone, methylene*iso*butylmethyl ketone, mesityl oxide and *iso*propenylethyl ketone with *iso*butylene at a temperature of from —40 to —100° usually copolymerize to rubber-like products [346].

Divinyl, *iso*prene and piperylene are easily copolymerized with *cyclo*pentadiene and methyl*cyclo*pentadiene in the presence of $BF_3 . O(C_2H_5)_2$ at a temperature of from —40 to —60° [347]. Divinyl [348, 349], *cyclo*pentadiene and 1,3-di*cyclo*hexadiene [350] with the terpenes myrcene, ocimene and allocimene in the presence of BF_3 form terpene resins which are stable to water and alkalis, soluble in drying oils and have a high viscosity. Divinyl copolymerizes with vinylbutyl ether in the presence of $BF_3 . O(C_2H_5)_2$ [189].

With styrene, vinyl acetate and *iso*propenyl acetate in the presence of BF_3, acenaphthylene forms copolymers with softening points of 150, 180 and 160° respectively [158, 159]. Styrene may be copolymerized with 1,2-dimethoxyethylene in the presence of $BF_3 . O(C_2H_5)_2$ [199] and with methyl methacrylate in the presence of BF_3 [350]. Vinylmethyl ether copolymerizes with vinyl*iso*butyl ether [184]. Vinyl acetate, mixed with the equivalent volume of thiophene and 2 per cent by weight of $BF_3 . O(C_2H_5)_2$ forms resin-like elastic copolymers [351].

In the presence of BF_3 or $BF_3 . O(C_2H_5)_2$ vinyl chloride can also be copolymerized with allyl ether (2—4 per cent), methyl methacrylate and vinyl methacrylate [352]; and 2-vinylfluorene with styrene, indene and acrylonitrile [353].

Styrene [354], *cyclo*pentadiene [355], myrcene or *allo*ocimene [356], on heating with unsaturated fatty acids or esters (linseed or soya bean oils) in the presence of BF_3, are converted into viscous or solid copolymers which are used as synthetic glues.

Polyvinyl acetals (polyvinyl butyral, polyvinyl formal) on heating with glyceridic oils and BF_3 give resin-like products [357]; *m*- and *p*-vinylphenyl *iso*cyanates in the presence of 1 per cent $BF_3 . O(C_2H_5)_2$ at a temperature of 20° copolymerize to viscous products [358].

It is recommended that coumarone and formaldehyde resins be treated with hydrocarbons from the cracking of petroleum, which contain olefines, in the presence of BF_3 for improving their quality [359].

Boron fluoride is used as a polymerization catalyst in technological processes (manufacture of poly*iso*butylene and polyvinyl ethers) and in scientific research work; the field of use of this catalyst continues to extend because, with the help of boron fluoride, olefines, diene hydrocarbons, terpenes and various unsaturated compounds are readily polymerized; moreover the polymerization proceeds selectively without the formation of secondary products, and can be directed, depending on the reaction conditions, to the formation of low-molecular or high-molecular polymers.

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CHAPTER VII

THE ADDITION OF ORGANIC SUBSTANCES CONTAINING OXYGEN OR SULPHUR TO ETHYLENIC COMPOUNDS

1. ADDITION OF WATER AND ALCOHOLS TO OLEFINES

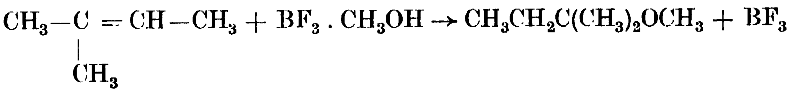
There are no reports of original investigations on the hydration of olefines in the presence of boron fluoride, so that although this question is of considerable scientific and practical interest, its examination had unfortunately to be limited to the patent literature.

According to the data contained in certain patents, ethylene adds on water comparatively easily in the presence of boron fluoride trihydrate at a temperature of 120—150° and a pressure of 25—900 atm [1].

The hydration proceeds well when ethylene is treated with a mixture of boron fluoride and aqueous hydrofluoric acid at a temperature of 200—300° and a pressure sufficient to keep the mixture in the liquid state [2].

Propylene is converted by boron fluoride hydrate into *iso*propyl alcohol and partially into *iso*propyl ether [3, 4].

The lower alcohols add on to olefines having tertiary carbon atoms in the presence of boron fluoride at ordinary pressure and a temperature below 100°. The reaction proceeds easily when the alcohols are used as coordination compounds with boron fluoride [5, 6]. Trimethylethylene is methoxylated with the formation of methylamyl ether according to the reaction



$$\underset{\displaystyle CH_3}{CH_3-\overset{|}{C}}=CH-CH_3 + BF_3 . CH_3OH \rightarrow CH_3CH_2C(CH_3)_2OCH_3 + BF_3$$

*iso*Butylene adds on methyl alcohol and gives *tert.*-butylmethyl ether [7]. Similarly propylene adds on ethyl alcohol [8] and ethylene glycol, [9] with the formation of the corresponding ethers. Such addition of alcohols in the presence of a BF_3 catalyst is apparently possible also for cyclic olefines.

The lower alcohols add on to vinylmethyl ketone in the presence of $BF_3O(C_2H_5)_2$, forming 4-alkoxy-2-butanones [10]:

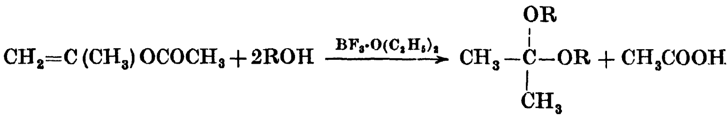
$$CH_3COCH = CH_2 + ROH \rightarrow CH_3COCH_2CH_2OR$$

Vinyl esters of carboxylic acids react with primary and secondary alcohols in the presence of BF_3 and HgO or coordination compounds of boron fluoride with alcohols in such a way that the hydrogen is directed to the $CH_2 =$ group, and two alkoxyl residues are added to the $= CH -$

group with simultaneous splitting off of an acid residue. As a result acetals are obtained :

$$CH_2=CHOCOR' + 2BF_3ROH \rightarrow CH_3CH(OR)_2 + R'COOH + 2BF_3$$

On heating, for example, vinyl acetate, methyl alcohol, $BF_3.CH_3OH$ and HgO 1 hr at 60°, methyl acetal is obtained with a yield of 99 per cent [11, 12]. *n*-Butyl alcohol adds on to vinyl acetate in the presence of $BF_3 . O(C_2H_5)_2$ and HgO with the formation of dibutylacetal with a yield of 88·5 per cent [13], but *tert.*-butyl alcohol in a similar reaction gives *iso*butylene, *tert.*-butyl acetate and other products. Primary and secondary alcohols with *iso*propenyl acetate in the presence of $BF_3 . O(C_2H_5)_2$ form ketals [14] according to the scheme

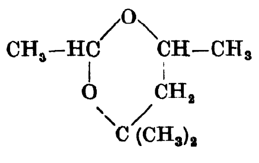


$$CH_2{=}C(CH_3)OCOCH_3 + 2ROH \xrightarrow{BF_3\cdot O(C_2H_5)_2} CH_3{-}\overset{OR}{\underset{CH_3}{C}}{-}OR + CH_3COOH$$

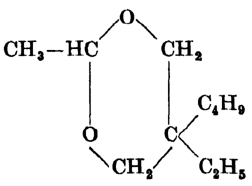
When vinyl esters of carboxylic acids are made to react with polyhydric alcohols in the presence of coordination compounds of boron fluoride with alcohols, ethers or acids, then, depending on the conditions, cyclic acetals with five- or six-membered rings, acetals with hydroxyl groups, or resins are obtained [13, 15].

Glycols with excess of vinyl esters at a temperature of 30—60° give hemiacetals of the esters $CH_3CH(OR')OCOR$, which are capable of reacting with another molecule of glycol and forming hydroxyalkylacetals. Ethylene glycol and vinyl acetate, heated to 45—50° with $BF_3 . CH_3OH$ and HgO form 2-methyl-1,3-dioxolane. Replacement of the vinyl acetate by vinyl propionate or butyrate gives one and the same cyclic acetal.

Propanediol-1,3 with vinyl acetate in the presence of $BF_3 . CH_3OH$ and HgO at 50—55° forms 2-methyl-1,3-dioxane and a small quantity of $CH_3CH(CH_2CH_2CH_2OH)_2$. 2-Methyl-pentanediol-2,4 and vinyl acetate in the presence of $BF_3 . C_4H_9OH$ and HgO at a temperature of 55° give 2,4,4,6-tetramethyl-1,3-dioxane (I). 2,2-Dimethylolheptane $CH_3CH_2C.(CH_2OH)_2CH_2CH_2CH_2CH_3$ and vinyl acetate in the presence of $BF_3.CH_3OH$ and HgO at a temperature of 60° form 2-methyl-5-ethyl-5-butyl-1,3-dioxane (II).



(I)

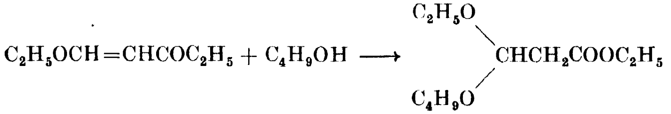


(II)

Diethylene glycol and tetraethylene glycol react in a similar way with vinyl acetate. The tendency towards the formation of cyclic acetals increases with increase of branching of the carbon atoms of the glycols [15].

Halohydrins add on to vinyl esters of carboxylic acids with the formation of halogen substituted acetals [16]. For example, ethylene glycol chlorohydrin and vinyl acetate with $BF_3 . CH_3OH$ and HgO at a temperature of 48° give β,β-dichlorodiethyl acetal.

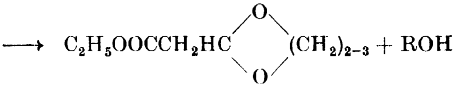
Boron fluoride ethyl etherate is a good catalyst also for the addition of alcohols to esters of a β-alkoxyacrylic acid [17, 18]. If a mixture of ethyl β-ethoxyacrylate (72 g), butyl alcohol (37 g) and $BF_3 . O(C_2H_5)_2$ (5 ml) is left for 8—12 hr at room temperature and then treated in a suitable way, ethyl β-ethoxy-β-butoxypropionate is obtained with a yield of 79 per cent (86 g):



$$C_2H_5OCH{=}CHCOC_2H_5 + C_4H_9OH \longrightarrow (C_2H_5O)(C_4H_9O)CHCH_2COOC_2H_5$$

With ethyl alcohol in these conditions ethyl β,β-diethoxypropionate is formed with a yield of 72 per cent. 1,2- and 1,3-Glycols add on to ethyl β-alkoxyacrylate in the presence of $BF_3 . O(C_2H_5)_2$ [19] according to the reaction

$$HO\,(CH_2)_{2-3}OH + ROCH{=}CHCOOC_2H_5 \longrightarrow$$



$$\longrightarrow C_2H_5OOCCH_2HC\langle O_2 \rangle(CH_2)_{2-3} + ROH$$

2. REACTIONS OF ETHYLENIC COMPOUNDS WITH ACETALS, ALKYL HALIDES, ANHYDRIDES AND ALDEHYDES

Boron fluoride ethyl etherate proved to be the best catalyst for the reaction of olefines [20] and vinylalkyl ethers [21, 22] with acetals. Also in the case of olefines the reaction proceeds in some directions with the formation of mixtures of products formed by the normal addition of acetals at the double bond of the olefines, and condensation products of acetals at the expense of the mobile hydrogen atoms of the methyl radicals which are connected with the carbon atoms with the double bond, as follows from the data of Table 72.

The reaction of acetals with vinyl alkyl ethers proceeds in such a way that the alkoxy group adds on to the least hydrogenated carbon with a double bond, and all the rest of the acetal is directed to the most hydrogenated carbon atom [21]. For example, dimethylacetal and vinylmethyl

Table 72. *Condensation of acetals with olefines* [20]

Reagent		Reaction product	Yield (%)
Olefine	Acetal		
$(CH_3)_2C = CH_2$	$CH_3CH(OC_2H_5)_2$	$C_2H_5OC(CH_3)_3$	39·0
		$CH_2 = C(CH_3)CH_2CH(CH_3)OC_2H_5$	13·0
		$(CH_3)_2C(OG_2H_5)CH_2CH(CH_3)OC_2H_5$	15·5
		$[CH_3CH(OC_2H_5)CH_2]_2C = CH_2$	2·5
$(CH_3)_2C = CH_2$	$CH_3CH_2CH_2CH(OCH_3)_2$	$CH_3OC(CH_3)_3$	42·0
		$CH_2 = C(CH_3)CH_2CH(OCH_3)CH_2CH_2CH_3$	11·0
		$(CH_3)_2C(OCH_3)CH_2CH(OCH_3)CH_2CH_2CH_3$	21·5
Mixture of $CH_2 = C(CH_3)CH_2C(CH_3)_3$ and $(CH_3)_2C = CHC(CH_3)_3$	$CH_3CH(OC_2H_5)_2$	$(CH_3)_2C(OC_2H_5)CH_2C(CH_3)_2CH_2CH_2CH_3$	3·0
		$(CH_3)_2CHCH(CH_3)C(CH_3)CH_2CH(CH_3)OC_2H_5$	52·0
$(CH_3CH_2)_2C = CH_2$	$CH_3CH(OC_2H_5)_2$	$CH_3CH = C(C_2H_5)CH_2CH(CH_3)OC_2H_5$	37·0
$(CH_3CH_2)_2C = CH_2$	$CH_3CH_2CH_2CH(OC_2H_5)_2$	$CH_3CH = C(C_2H_5)CH_2CH(OC_2H_5)CH_2CH_2CH_3$	27·0
$C_6H_5CH = CH_2$	$CH_3CH(OC_2H_5)_2$	$[CH_3CH(OC_2H_5)]_2CH_3$	35·0

ether in the presence of $BF_3 . O(C_2H_5)_2$ form 1,1,3-trimethoxybutane with a yield of 79 per cent [21]:

$$CH_2 = CHOCH_3 + CH_3CH(OCH_3)_2 \rightarrow CH_3CH(OCH_3)CH_2CH(OCH_3)_2$$

In addition to this, small quantities (10 per centof 1,1,3,5-tetramethoxyhexane,) formed by the condensation of the main product with a second molecule of acetal, are obtained.

With vinylmethyl ether the diethylacetal of butyraldehyde forms 1,3-diethoxy-1-methoxyhexane with a yield of 63·5 per cent of the theoretical and the dimethylacetal of benzaldehyde gives 3-phenyl-1,1,3-trimethoxypropane with a yield of 56 per cent of the theoretical [23].

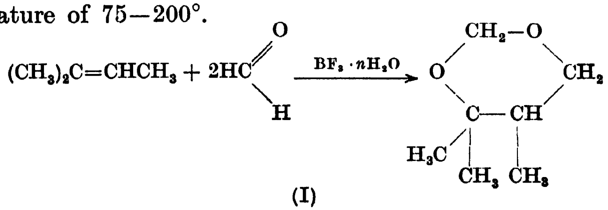
Ketals react easily with vinylmethyl ether [23]. The diethylketal of acetone and *cyclo*hexanol with vinylmethyl ether in the presence of $BF_3 . . O(C_2H_5)_2$ form 1,3-diethoxy-1-methoxy-1-methylbutane with 32 per cent yield and 1-ethoxy-1-(2-ethoxy-2-methoxyethyl) *cyclo*hexane respectively.

Vinylalkyl ethers with orthoesters in the presence of boron fluoride ethyl etherate are converted into acetals of dicarbonyl compounds [24]. For example, vinylmethyl ether and trimethoxymethane react according to a scheme such as this:

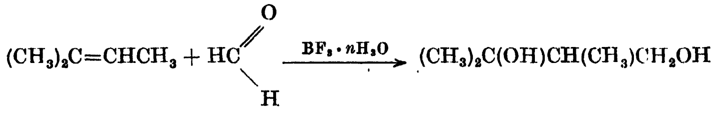
$$CH_3OCH = CH_2 + HC(OCH_3)_3 \xrightarrow{BF_3.O(C_2H_5)_2} (CH_3O)_2CHCH_2CH(OCH_3)_2$$

Schmerling [25] studied the reaction of *tert.*-butyl chloride with *cyclo*hexene in the presence of BF_3 and found that on passing 10 g BF_3 for $^1/_2$ hr into a solution of 185 g *tert.*-butyl chloride and 164 g *cyclo*hexene, cooled in ice and stirred, 1-chloro-1-*tert.*-butylcyclohexane, chloro*cyclo*hexane and 1-*tert.*-butyl*cyclo*hexane are obtained in yields of 23, 15 and 12 per cent respectively. There are no other investigations on the use of BF_3 for similar reactions.

Olefines can enter into reaction with formaldehyde in the presence of boron fluoride hydrates [26—29]. In addition, depending on the temperature, time and composition of the catalyst, 1,3-dioxanes (I), 1,3-diols (II) or dienic hydrocarbons (III) are obtained. The first are formed by using the olefine and aldehyde in 1 : 2 ratio, and a catalyst of composition 1 mole BF_3 to 9—25 moles water at a temperature of 10—75°. 1,3-Diols and diolefines are obtained with equimolecular quantities of the reagents with a catalyst of composition 1 mole BF_3 to 25—125 moles water at a temperature of 75—200°.

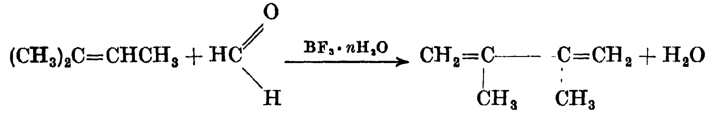


(I)



$$(CH_3)_2C{=}CHCH_3 + HC\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}} \xrightarrow{BF_3 \cdot nH_2O} (CH_3)_2C(OH)CH(CH_3)CH_2OH$$

(II)



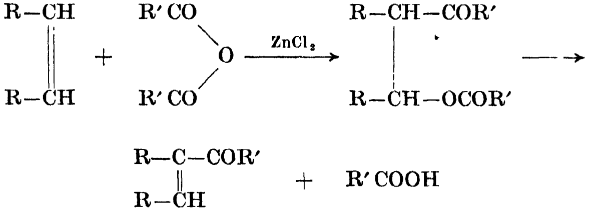
$$(CH_3)_2C{=}CHCH_3 + HC\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}} \xrightarrow{BF_3 \cdot nH_2O} CH_2{=}\underset{\displaystyle CH_3}{C}{-}\underset{\displaystyle CH_3}{C}{=}CH_2 + H_2O$$

(III)

Vinyl alkyl ethers with aldehydes in ratios of 1 : 2 or 1 : 4 in the presence of BF_3 form complex acetals which on hydrolysis with acids are converted into α,β-unsaturated aldehydes having in their composition two carbon atoms more than the original aldehyde [30]. Thus, if 148 g vinylmethyl ether is slowly added to a mixture of 636 g benzaldehyde and 0·375 ml $BF_3 . O(C_2H_5)_2$ at a temperature of 20—30° an acetal is formed which on hydrolysis gives cinnamic aldehyde with a yield of 60 per cent and methyl alcohol.

Olefines of the di*iso*butylene type and diketene in the presence of BF_3 form unsaturated diketones [31].

I. L. Kondakov [32], and later A. P. Meshcheryakov and L. V. Petrova [33], found that olefines react with acid anhydrides in the presence of $ZnCl_2$ according to the scheme



$$\begin{matrix} R{-}CH \\ \| \\ R{-}CH \end{matrix} + \begin{matrix} R'CO \\ \quad\rangle O \\ R'CO \end{matrix} \xrightarrow{ZnCl_2} \begin{matrix} R{-}CH{-}COR' \\ | \\ R{-}CH{-}OCOR' \end{matrix} \longrightarrow \begin{matrix} R{-}C{-}COR' \\ \| \\ R{-}CH \end{matrix} + R'COOH$$

It is probable that in the presence of a boron fluoride catalyst the conversion takes place in just the same way, but the ketoester first formed in the presence of BF_3 easily dissociates into an unsaturated ketone and acid, and has therefore not been observed by investigators. In the presence of BF_3 cyclic or iso-olefines react particularly readily with anhydrides of carboxylic acids containing 2—6 atoms of carbon [34]. Di*iso*butylene, *iso*nonylene and *iso*decylene enter into reaction at room temperature. *cyclo*Hexene and acetic anhydride form tetrahydroacetophenone as final product [35].

3. ADDITION OF CARBOXYLIC ACIDS TO OLEFINES AND THEIR SUBSTITUTED DERIVATIVES

The possibility of the addition of organic acids to olefines was foretold by N. A. Menshutkin [36—38] more than seventy years ago in his remarkable investigation on the dissociation of esters of tertiary alcohols to acid and olefine. In practice this reaction was first carried out by D. P. Konovalov [39, 40] in effecting the addition of acetic and chloracetic acids to olefines with a tertiary carbon atom.

I. L. Kondakov [41, 42] used a zinc chloride catalyst to accelerate the reaction and in this way he set a beginning to the study of the catalytic addition of acids to tertiary olefines.

In recent decades other halides, phosphates and sulphates of metals, and also mineral acids, have been tested as catalysts for the addition of acids to olefines. Their chief disavantage is low catalytic activity which permits esters to be obtained with a yield not exceeding 30 per cent of the theoretical.

Boron fluoride was first tested as a catalyst in the addition reaction of carboxylic acids to olefines by Nieuwland and collaborators [43], who found that on passing propylene for 16 hr at a temperature of 70° and a pressure of 250 mm above atmospheric into a mixture of 3 g BF_3 and 1 mole acetic, chloro-, dichloro- and trichloro acetic acids, the *iso*propyl ester of the corresponding acid is obtained with a yield of 7, 34, 39 and 49 per cent.

This reaction was studied in detail over many years by S.V. Zavgorodnii. He studied the reaction of 13 organic acids (5 aliphatic monobasic, 3 dibasic, 2 aromatic and 3 haloacetic) with 18 unsaturated compounds (6 olefines, 1 cyclo-olefine, 1 arylolefine, 3 halo-olefines, 2 alkylvinyl ethers, 3 allylalkyl ethers, 1 terpene and 1 dienic hydrocarbon). As a result of these investigations it was shown that boron fluoride was a very active catalyst for the addition of organic carboxylic acids to ethylenic compounds. It may be used either independently or as a coordination compound with ethers, or with organic and mineral acids. When there is no great necessity to study the quantitative side of a process, boron fluoride may be used independently or as a coordination compound with acetic acid. However, boron fluoride ethyl etherate, which enables the addition of acids to ethylene compounds to be carried out in relatively mild conditions which do not bring about side reactions (mainly the polymerization of olefines), and enables esters to be obtained with a yield of 40—95 per cent, is the best catalyst in all respects [44]. Addition of red mercury oxide to boron fluoride ethyl etherate increases the polymerizing effect on the olefines and slightly lowers the total ester yield 44.

Olefines add on acids at the double bond according to K. V. Markownikov's rule. In the case of olefines with two equivalently substituted carbon atoms at the double bond, for example pentene-2, the addition of acids proceeds mainly according to the Zaitsev—Wagner rule, i. e. in such a way that the acid residue is directed to the carbon atom linked to the methyl radical.

The rate of addition of organic acids to ethylene compounds and the capacity for ester formation in the presence of boron fluoride ethyl etherate depend on a number of factors.

The chemical nature and structure of compounds with an ethylenic bond often predetermine not only the course but also the direction of the reaction. In the series of *n*-olefines the activity increases from ethylene to the butylenes. Then it begins to fall again to pentene-2 and hexene-2.

Ethylene in the gaseous state reacts very poorly with acids in the presence of $BF_3 . O(C_2H_5)_2$. Even with such a strong acid as bromoacetic, in dichlorethane as solvent at a temperature of 40—50°, ethyl bromoacetate is obtained with a yield of 8 per cent of the theoretical.

Hexene-2 adds organic acids even more slowly. On heating it with chloroacetic acid in the presence of $BF_3 . O(C_2H_5)_2$ at 97° for 2 hr, the yield of *sec.*-hexyl chloroacetate amounts to 5 per cent of the theoretical.

Of the three butylenes a hydrocarbon of iso-structure, *iso*butylene, possesses the highest chemical activity. But it is easily polymerized in the presence of boron fluoride ethyl etherate. Therefore at a temperature of 50 and 97°, instead of the expected esters, polymers of *iso*butylene are formed. At room temperature *iso*butylene and acetic acid, in the course of 2 hr, form *tert.*-butyl acetate with a yield of 59 per cent. This yield remains constant for several hours. Then it begins to fall and on heating for 24 hr, owing to the dissociation of the ester it decreases to 25 per cent.

After *iso*butylene in activity comes pseudobutylene which among the normal olefines is the most active in the addition of acids. When heated at a temperature of 97° for 24 hr with acetic and benzoic acids in the presence of $BF_3 . O(C_2H_5)_2$ it gives the *sec.*-butyl esters of these acids with a yield corresponding to 66 and 89 per cent. With trichloroacetic acid at 97° after 2 hr *sec.*-butyl trichloroacetate is obtained in a yield of 91 per cent.

a-Butylene approaches pseudobutylene in its activity and with all acids it also gives the *sec.*-butyl ester, but in lower yield.

Pentene-2 adds on organic acids less vigorously than the butylenes, but more readily than ethylene and hexene-2 [45]. When heated at 97° for 24 hr with acetic, oxalic, benzoic and trichloroacetic acids it gives a yield of esters of 40, 27, 53 and 59 per cent respectively. With trichloroacetic acid a yield of 68 per cent is reached in the course of 2 hr [44],

*cyclo*Hexene, with acetic, trichloroacetic and bromoacetic acids in corresponding conditions, forms esters almost with the same yield as pseudobutylene. The yield of *cyclo*hexyl acetate at 97° after 73 hr reaches 60 per cent and of *cyclo*hexyl trichloroacetate at 50° after 25 hr 86 per cent the theoretical [46, 47].

Halo-olefines with halogen on the carbon not connected to the double bond have a decreased capacity for adding organic acids at the double bond. Allyl bromide, in general, practically does not add on acetic acid at a temperature of 97°. Crotyl bromide and *iso*butenyl chloride add on acids, although with difficulty, with the formation of the corresponding esters. It is characteristic that the introduction of a chlorine atom into *iso*butylene lowers its activity to polymerization in the presence of boron fluoride ethyl etherate [48]. In Table 73 the maximum yields of esters obtained by the addition of acids to olefines in the presence of boron fluoride ethyl etherate catalyst are given.

The stronger the organic acids the more readily do they add on to an ethylenic bond. In the series of aliphatic monobasic acids, formic and acetic acids add on more readily than the others, then come propionic, *n*-butyric and *iso*valeric [44]. Thus, the capacity of the acids to add to the double bond decreases in proportion to the increase of the hydrocarbon residue connected to the carboxyl group. Dibasic saturated aliphatic acids are chemically less active and add on to the double bond with more difficulty than the corresponding monobasic acids. The activity in this series decreases from oxalic to succinic acid. However, in the presence of boron fluoride ethyl etherate these acids also add on to olefines and give high yields of esters. Thus, oxalic acid with pseudobutylene at 97° after 24 hr forms di-*sec.*-butyl oxalate with a yield of 30 per cent, and succinic acid, at the same temperature but after 62 hr, gives di-*sec.*-butyl succinate with a yield of 28 per cent.

Aromatic acids are chemically more active than aliphatic, and add on more easily to ethylenic compounds. Whereas acetic acid with pseudobutylene at 97° after 24 hr forms *sec.*-butyl acetate with a yield of 63 per cent, benzoic acid gives an ester with a yield of 89 per cent, oxalic 29 per cent and phthalic 48 per cent.

Halogen substituted acetic acids show the greatest chemical activity. They add on very easily at the double bond even at room temperature. Their activity falls from the chloroacetic acids to bromoacetic. In the chloroacetic acids the activity increases with increase in the number of chlorine atoms. But halogen substituted acetic acids, as strong acids, are capable at increased temperature of saponifying the esters formed, and increase the polymerizing activity of the catalyst. As a result of this, when they are made to react with olefines such as pseudobutylene and pentene-2 at 97°, and in part at 50°, for the first 2—4 hr the reaction proceeds with the formation of the maximum yield of esters. After this, *Table* 73. *Maximum yields of esters obtained by adding acids to olefines in the presence of boron fluoride ethyl etherate*

Olefine	Acid	Reaction temperature (°C)	Time (hr)	Ester	Yield of ester (%)
Ethylene	Bromoacetic	Room	—	Ethyl bromoacetate	8
Pseudobutylene	Acetic	97	24	*sec.*-Butyl acetate	68
Pseudobutylene	Propionic	97	24	*sec.*-Butyl propionate	59
Pseudobutylene	*n*-Butyric	97	24	*sec.*-Butyl butyrate	41
Pseudobutylene	*iso*Valeric	97	24	*sec.*-Butyl *iso*valerate	41
Pseudobutylene	Oxalic	150	2	Di-*sec.*-butyl oxalate	41
Pseudobutylene	Succinic	150	4	Di-*sec.*-butyl succinate	47
Pseudobutylene	*d*-Tartaric	150	2	Di-*sec.*-butyl tartrate	43
Pseudobutylene	Benzoic	97	24	*sec.*-Butyl benzoate	91
Pseudobutylene	Phthalic	150	4	Di-*sec.*-butyl phthalate	63
Pseudobutylene	Chloroacetic	16—25	128 days	*sec.*-Butyl chloroacetate	88
Pseudobutylene	Trichloroacetic	52	4	*sec.*-Butyl trichloroacetate	94
α-Butylene	Acetic	97	8	*sec.*-Butyl acetate	52
α-Butylene	Chloroacetic	50	24	*sec.*-Butyl chloroacetate	77
*iso*Butylene	Acetic	12—16	2	*tert.*-Butyl acetate	61
*iso*Butylene	Oxalic	12—16	24	Di-*tert.*-butyl oxalate	13
*iso*Butylene	Benzoic	50	24	*tert.*-Butyl benzoate	14
β-Amylene	Acetic	97	24	*sec.*-Amyl acetate	41
β-Amylene	Oxalic	97	24	Di-*sec.*-amyl oxalate	27
β-Amylene	Benzoic	97	24	*sec.*-Amyl benzoate	54
β-Amylene	Chloroacetic	50	24	*sec.*-Amyl chloroacetate	65
β-Amylene	Trichloroacetic	50	24	*sec.*-Amyl trichloroacetate	88
β-Hexylene	Chloroacetic	97	2	*sec.*-Hexyl chloroacetate	6
*cyclo*Hexene	Acetic	97	72	*cyclo*Hexyl acetate	63
*cyclo*Hexene	Bromoacetic	50	6	*cyclo*Hexyl bromoacetate	80
*cyclo*Hexene	Trichloroacetic	50	34	*cyclo*Hexyl trichloroacetate	90
Styrene	Bromoacetic	Room	23 days	α-Phenylethyl bromoacetate	15
*iso*Butenyl chloride	Acetic	78—80	8·5	Chloro*iso*butyl acetate	29

the ester begins to be saponified and on further heating the yield of ester falls. In addition the process of polymerization of olefines is intensified. *cyclo*Hexyl esters of organic acids are more stable, and in the conditions studied are not subject to saponification [46].

The temperature and duration of the reaction exert an enormous influence on the addition of organic acids to olefines. As a rule a rise in temperature and an increase in the time of reaction increase the yield of esters. Rise in temperature and increase in the time of reaction are, however, positive factors only up to a certain limit. This limit depends both on the acid and on the ethylenic compound. For ethylene, *n*-butylenes, pentene-2 and aliphatic monobasic unsubstituted acids a temperature of 100° is more favourable. At a lower temperature the reaction goes slowly and at a higher one appreciable polymerization of the olefines takes place, and the total yield of esters is diminished. Acetic acid, for example, hardly reacts at all with pseudobutylene at room temperature. At 52° after 48 hr the yield of *sec.*-butyl acetate amounts to 51 per cent and at 97° after 24 hr the ester is obtained with a very high yield (62—63 per cent of the theoretical). At 165° the maximum yield of ester, 50 per cent, is attained after 2 hr and remains the same for 24 hr.

For the addition of dibasic aliphatic and aromatic acids it is best to assume a temperature of from 100 to 150°, because below 100° they add on comparatively slowly at the double bond [44]. At 150° after 2 hr oxalic, succinic, D-tartaric and phthalic acids add on to pseudobutylene with the formation of di-*sec.*-butyl esters with a yield of 40, 37, 42 and 48 per cent respectively. True, the addition of D-tartaric acid is also accompanied by polymerization of the olefines.

In the reaction of *n*-butylenes and pentene-2 with halogen substituted acetic acids a higher yield of esters is reached at room temperature. Thus, pseudobutylene with chloroacetic acid forms in the course of 128 days, *sec.*-butyl chloroacetate with a yield of 86 per cent. With trichloroacetic acid after 96 hr the yield of *sec.*-butyl trichloroacetate amounts to 93 per cent. Pentene-2 with trichloroacetic acid in the course of 24 hr forms *sec.*-amyl trichloroacetate with a yield of 57 per cent. Increase of temperature to 97°, as already noted, promotes the saponification of the esters formed and intensifies the polymerization of the olefines. Thus, in these conditions rise of temperature and increase in the time of reaction will be negative factors. In working with *iso*butylene and with styrene increase of temperature should be avoided because of their vigorous polymerization in the presence of boron fluoride ethyl etherate. The addition of certain acids to these hydrocarbons (acetic acid to *iso*butylene and bromoacetic to styrene) can be brought about with positive results only at room temperature.

An increase in the quantity of boron fluoride ethyl etherate catalyst to 9 per cent in the reaction with unsubstituted olefines accelerates the esterification and increases the total yields of esters. The use of boron fluoride ethyl etherate in a quantity greater than 9 per cent does not accelerate the reaction and does not increase the yield of esters, but intensifies the process of polymerization of olefines.

According to the results of Wunderly and Sowa [49], in the reaction of *cyclo*hexene with acetic acid in the presence of free BF_3 the yield of *cyclo*hexylacetate is increased when the quantities of catalyst are increased up to 6 per cent. A higher percentage of boron fluoride (up to 18 per cent) does not increase the yield of ester.

The ratio of the original reagents exerts a substantial influence on the reaction. A small excess of olefines usually increases the total yield of ester at corresponding temperatures and identical time of reaction. Pseudobutylene, for example, with acetic acid in 1 : 1 ratio and a temperature of 97° after 24 hr forms *sec.*-butyl acetate with a yield of 62 per cent, but in 1·5 : 1 ratio with a yield of 66 per cent. Pentene-2 with trichloroacetic acid in 1 : 1 ratio and a temperature of 50° after 24 hr gives 85 per cent *sec.*-amyl trichloroacetate, but in 4·5 : 1 ratio and the same conditions, 95 per cent.

The order of introduction of the reagents and catalyst into the reaction is also of significance. In working with low-boiling olefines it is convenient to introduce first the acid, then the catalyst, and finally to add the olefine. But for styrene and α-pinene this order of introducing the reagents immediately produces a brisk reaction and vigorous boiling of the mixture leading to the formation of polymerization products, and in the worst case to explosion of the reacting mixture. Therefore, when working with these hydrocarbons it is necessary to add the catalyst to the cooled mixture of hydrocarbon and acid in small portions with frequent stirring.

The rate of reaction and yield of ester depend on the capacity of the reacting acids to dissolve or mix with olefines. The better the acid dissolves or mixes with the olefine, the quicker the reaction proceeds, and the lower is the temperature required and the less prolonged is the time necessary for reaching the maximum yield of ester.

In those cases when the original reagents do not intermix, it is useful to use solvents which would act as homogenizers or diluents for the reaction mixture.

In the addition, for example, of acetic and trichloroacetic acids to *cyclo*hexene it was found [50] that neutral solvents, benzene and carbon tetrachloride, by their presence moderate the reaction and decrease its rate somewhat, especially at high dilution. They do not, however, have any substantial influence on the total yield of ester. In an ionizing solvent and particularly in acetone, the addition of trichloroacetic acid to *cyclo*hexene in the presence of boron fluoride ethyl etherate becomes appreciable only 20—30 hr after the beginning of the experiment.

The state of aggregation of the ethylenic compounds is also of significance. The reaction proceeds most readily with liquid compounds. Carrying out the reaction with gaseous olefines (ethylene and pseudobutylene) at atmospheric pressure greatly retards it and probably contributes to polymerization. Stirring or shaking the reaction mixture accelerates the addition of acids to ethylenic compounds.

The material of the reaction vessel also plays an important part. The most suitable is glass apparatus. Autoclaves of good steel do not differ appreciably in this respect from glass flasks. But to carry out the reaction in an iron autoclave, especially with halogen-substituted acetic acids, reduces its rate, lowers the total yield of esters and favours the polymerization of the olefines. For example, pentene-2 with trichloroacetic acid at a temperature of 50—60° forms after 2 hr *sec.*-amyl trichloroacetate, in a glass flask with a yield of 85 per cent, but in an iron autoclave with a yield of 55 per cent.

A still more active catalyst for the addition of aliphatic acids to olefines is boron fluoride with anhydrous hydrofluoric acid, as is seen from Table 74 in which the yield of *iso*propyl acetate obtained in the presence of different catalysts [51] is given, and from Table 75.

A great disadvantage of the BF_3—HF catalyst is its strong corrosive action on the metal of the reaction bomb. In one of the experiments it was found that the BF_3 was more than 90 per cent converted into the fluoroborate mainly of iron. Besides this, the reaction is accompanied by the formation of alkyl fluorides.

Table 74. Addition of acetic acid to propylene in the presence of different catalysts [51]

Catalyst	Concentration of catalyst (%)	Reaction temperature (°C)	Time of reaction (hr)	Yield of propyl acetate (%)
$ZnCl_2$	6	150	2	5
$AlCl_3$	6	100	5	0
$AlCl_3 + HCl$	6	100	3	0
H_2SO_4	6	150	5	5
$HOSO_2Cl$	3	100	2	5
HBF_4	3	100	1·5	40
$BF_3 + H_2SO_4$	3	150	5	60
$BF_3 + HCl$	3	100	0·5	64
$BF_3 + HF$	3	100	0·5	80
BF_3 HF	3 1	100	0·5	57

Table 75. *Addition of acetic acid to olefines in the presence of the catalyst* BF_3—HF [51]

Olefine	Concentration of catalyst (%)	Reaction temperature (°C)	Time of reaction (hr)	Ester	Yield (%)
Ethylene	10	150	3	Ethyl acetate	50
Propylene	3	90—100	0·5	*iso*Propyl acetate	80
Butene-1	3	60	1	*sec.*-Butyl acetate	50
Pentene-1	3	60	1	*sec.*-Amyl acetate	52
*cyclo*Hexene	3	100	1	*cyclo*Hexyl acetate	62
Allyl chloride	6	150	2	β-Chloro*iso*propyl acetate	32

In recent times many patent claims have been made for the use of boron fluoride, free [52, 53] or as dihydrate [54], coordination compounds with organic acids [55], or, together with hydrofluoric acid [56—58], as a catalyst for the addition of carboxylic acids to ethylene [54, 56, 59], propylene [57], amylenes [53, 54], methyl*cyclo*pentene [57] and olefino-paraffinic hydrocarbon mixtures [55].

Nieuwland and collaborators studied the reaction of substituted aromatic carboxylic acids with olefines in the presence of boron fluoride [60—64] and found that the presence in the benzene ring of such substituents as hydroxyl groups strongly activates the hydrogen atoms of the benzene ring. Therefore, *o*-, *m*- and *p*-hydroxybenzoic acids with propylene in the presence of BF_3 form, besides the *iso*propyl esters of these acids, acids and esters alkylated in the ring. It is considered probable that the alkylation of the benzene ring of salicylic acid proceeds by way of the isomerization, under the influence of boron fluoride [60, 64, 65], of the complex salicylate formed, but *p*-hydroxybenzoic acid adds to olefines at the hydroxyl group and forms an ether [61], by the isomerization of which derivatives substituted in the ring are obtained. *m*-Hydroxybenzoic acid is alkylated in a similar way.

The highest yields of alkyl salicylates are obtained with primary olefines and the lowest in the reaction with tertiary olefines [66].

In these reactions boron fluoride may be used in the form of a coordination compound [67]. Instead of individual olefines, the olefine-rich gases of vapour-phase cracking may be used. But in this case a complex mixture of products, which may be used as lubricating materials [68], is obtained with salicylic acid.

It is interesting to observe that *p*-hydroxybenzoic acid, in the same way as its ethyl ester, with *cyclo*hexene and *cyclo*pentene in the presence of BF_3 and at a temperature of 50° forms the corresponding *p-cyclo*alkoxybenzoic acids [69], i. e. the phenolic hydroxyl in this case is probably more reactive than the carboxyl group.

Halogen and nitro-substitued aromatic carboxylic acids react with olefines with more difficulty, and the reaction proceeds only to the formation of esters, as with benzoic acid. For example, *o*-chlorobenzoic acid with propylene in the presence of BF_3 in *iso*propyl acetate, in the course of 72 hr gives *iso*propyl *o*-chlorobenzoate with a yield of 45 per cent [6]. *p*-Nitrobenzoic acid adds on to propylene in tetrachloroethane with the formation of *iso*propyl *p*-nitrobenzoate with a yield of 14·5 per cent.

o- and *p*-Aminobenzoic acids do not add on to propylene in the presence of equimolecular quantities of BF_3 [62]. The absence of reaction is explained by the fact that boron fluoride reacts vigorously with the nitrogen of the amino group of the acid, forming a stable coordination covalent compound, and in this way is withdrawn from the sphere of catalytic action [70]. Therefore, in order to esterify these acids, for example with alcohols, it is necessary to use a catalyst in a quantity from 2 to 4·5 moles per 1 mole of acid [70].

According to the information of certain patents ethylene, amylenes, di*iso*butylene and other olefines add on hydrochloric acid in the presence of the catalyst $BF_3 . H_3PO_4$ [71] or $BF_3 . H_2O$ [72], giving high yields (89—96 per cent) of alkyl chlorides.

Anhydrous hydrofluoric acid easily adds on hydrogen fluoride to unsubstituted olefines without a catalyst. The use of BF_3 for the addition of HF to ethylene and propylene enables the corresponding alkyl fluorides to be obtained with the same yield as without a catalyst. But in the presence of BF_3 the reaction proceeds very vigorously and is accompanied by resin formation [73]. Therefore its use in this case is not necessary. In the case of polychloro- or polyfluoro-olefines (especially those containing CF_3 groups alongside the carbon atoms linked by the double bond) in which the activity of the double bond is greatly reduced, the presence of BF_3 appreciably activates the hydrofluorination. Thus, for example, in the reaction of 1,1,2-trichloroethylene (I) with HF in 1 : 2 molar ratio in the presence of BF_3, 1,1,2-trichloro-1-fluoroethane (II) is obtained in a yield of 56·5 per cent and 1,2-dichloro-1,1-difluoroethane (III) in a yield of 9 per cent of the theoretical [74, 75]. The reaction may be represented in the following way:

$$\underset{(I)}{2CHCl = CCl_2} + 3HF \xrightarrow{BF_3} \underset{(II)}{CH_2ClCCl_2F} + \underset{(III)}{CH_2ClCClF_2} + HCl$$

Trifluoropropylene $F_3CCH{=}CH_2$ does not react with HCl even in the presence of boron fluoride [76].

Activation with boron fluoride of the addition of HF to halo-olefines is no doubt dependent on the formation of the coordination complex HF . BF_3 in which the H—F link acquires an ionic character, which facilitates the separation of the proton and its addition to the more negative carbon atom at the double bond.

The Addition of Carboxylic Acids to Styrene

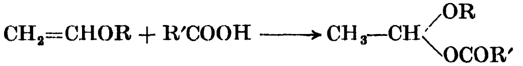
There are no original investigations on the reaction of styrene with carboxylic acids.

According to the data of one of the patents [77], styrene with acetic acid and formaldehyde in the presence of BF_3 at room temperature forms a diacetate of the following general formula:

$$CH_3COOCH_2(CH_2CHC_6H_5)_nOCOCH_3 \qquad (n = 1,2 \text{ or more})$$

The Reaction of Carboxylic Acids with Vinylalkyl and Allylalkyl Ethers

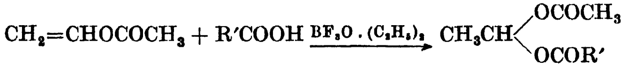
M. F. Shostakovskii and collaborators [78, 79] found that vinylalkyl ethers add on monocarboxylic acids in the presence of an orthophosphoric acid catalyst or without a catalyst with the formation of partial acylals almost in quantitative yield according to the reaction



$$CH_2{=}CHOR + R'COOH \longrightarrow CH_3{-}CH\begin{matrix} \diagup OR \\ \diagdown OCOR' \end{matrix}$$

S. V. Zavgorodnii [80] studied this reaction in the presence of a boron fluoride ethyl etherate catalyst and showed that ethers such as vinylethyl and vinyl *n*-butyl do not add on carboxylic acids in the presence of BF_3 . . $O(C_2H_5)_2$ and do not form acylals, but are broken down by them and give the alkyl esters of the corresponding acids and polymers of vinyl ethers. Thus, the cleavage proceeds more energetically the less strong the acid. Therefore the highest yields of esters are obtained for the weaker acids. For example, in the reaction of vinylethyl ether with acetic, chloroacetic and trichloroacetic acids the ethyl esters of those acids are obtained with yields of 85·8, 56·9 and 30 per cent respectively.

Vinyl acetate with carboxylic acids in the presence of boron fluoride ethyl etherate forms ethylidene esters [81] according to the scheme



$$CH_2{=}CHOCOCH_3 + R'COOH \xrightarrow{BF_3O\,.\,(C_2H_5)_2} CH_3CH\begin{matrix} \diagup OCOCH_3 \\ \diagdown OCOR' \end{matrix}$$

*iso*Propenyl acetate with carboxylic acids in the presence of BF_3 and mercury acetate undergoes the so-called vinylic change or acidolysis [82]. For example, 200 g *iso*propenyl acetate and 88 g butyric acid in the presence of 2 g mercury acetate and 1 ml BF_3 . $O(C_2H_5)_2$, when allowed to stand for 24 hr at a temperature of 20—25°, form 42 g *iso*propenyl butyrate according to the reaction

$$CH_2{=}C(CH_3)OCOCH_3 + C_3H_7COOH \xrightarrow{BF_3 . O(C_2H_5)_2} CH_2 = C(CH_3)OCOC_3H_7 + CH_3COOH$$

Allylalkyl ethers also do not add on organic acids in the presence of the catalyst $BF_3 . O(C_2H_5)_2$, but are split up by it and are converted into alkyl carboxylic esters and allyl alcohol. In this case the yields of esters are higher the stronger the acid.

In the series allylmethyl, allylethyl and allyl*iso*propyl ethers, judging from the yield of carboxylic esters formed, the cleavage proceeds more easily the less complex the alkyl radical of the ether.

Addition of Carboxylic Acids to Terpenes

Camphene with acetic and formic acids in the presence of boron fluoride forms *iso*bornyl esters of these acids in almost quantitative yield [83].

α-Pinene is easily polymerized in the presence of boron fluoride ethyl etherate. However, if the catalyst is added dropwise to a well cooled mixture of α-pinene and acids, then at room temperature the reaction proceeds mainly to the formation of the *iso*bornyl esters of the acids with a high yield [77]. If, however, the calculated amount of $BF_3 . O(C_2H_5)_2$ is added all at once, the reaction proceeds very vigorously with the formation of polymers of α-pinene as basic products. The reaction takes the same direction when the mixture is heated to a temperature of 97°.

In certain patents [84] it is recommended that pinene or abietic acid be condensed with aliphatic acids and higher alcohols or phenols in the presence of BF_3.

4. REACTIONS OF KETENE

Ketene, like olefines, in the presence of boron fluoride, chiefly in the form of etherates, adds on haloalkyl ethers, aldehydes, ketones and their various derivatives. Monochloromethyl ether, for example, adds to ketene with the formation of the chloroanhydride of β-methoxypropionic acid [85] according to the reaction

$$CH_3OCH_2Cl + CH_2{=}CO \xrightarrow{BF_3} CH_3OCH_2CH_2COCl$$

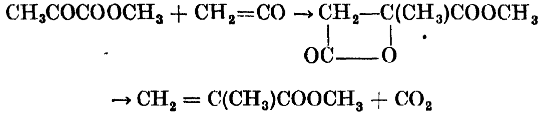
On adding ketene to a mixture of methyl formal and BF_3 with continuous stirring and cooling to −80°, methyl β-methoxypropionate is obtained with a yield of 73 per cent of the theoretical [86]:

$$CH_2(OCH_3)_2 + CH_2{=}CO \xrightarrow{BF_3} CH_3OCH_2CH_2COOCH_3$$

Similarly alkoxyacetals add on to ketene. Thus, on passing ketene into a mixture of methoxymethylacetal $CH_3OCH_2CH(OCH_3)_2$ and $BF_3 . O(CH_3)_2$ in absolute ether at a temperature of 1—2°, methyl β,γ-dimethoxybutryric acid is obtained with a yield of 89 per cent [87].

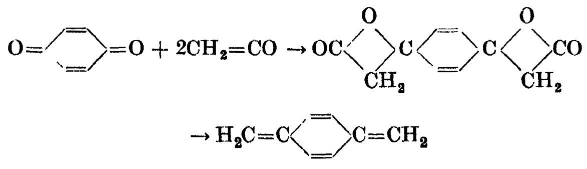
Saturated and unsaturated ketones and aldehydes with ketene form β-lactones or the corresponding unsaturated acids. Acetone, ketene and $BF_3O . (C_2H_5)_2$ at 20° give β,β-dimethylacrylic acid and *iso*propenylacetic acid [88]. Ketene with methacraldehyde in the presence of boron fluoride ethyl etherate in *iso*propyl ether at a temperature of 0—10° is converted into the β-lactone of 3-hydroxy-4-methyl-4-pentenoic acid [89]. If, instead of methacraldehyde, crotonaldehyde is taken, the β-lactone of hexenoic acid is obtained [90]. Unsaturated ketones and ketene in the presence of boron fluoride give lactones of the corresponding unsaturated acids [91]. Diketones may enter into reaction with one or two molecules of ketene in the presence of $BF_3 . O(C_2H_5)_2$ and form the mono- and dilactones of the corresponding acids, which when decarboxylated form unsaturated ketones and dienic hydrocarbons [92, 93].

Esters of ketonic acids with ketene and $BF_3 . O(C_2H_5)_2$ are converted into β-lactones, which on decarboxylation form unsaturated esters [92, 94, 95]. For methyl pyruvate the reaction may be represented by the scheme



$$\begin{array}{l} CH_3COCOOCH_3 + CH_2{=}CO \rightarrow \begin{array}{l} CH_2\text{—}C(CH_3)COOCH_3 \\ |\qquad\ \ | \\ OC\text{——}O \end{array} \\ \qquad\qquad\qquad \rightarrow CH_2 = C(CH_3)COOCH_3 + CO_2 \end{array}$$

Quinones, like diketones of the aliphatic series, react with two molecules of ketene in the presence of $BF_3 . O(C_2H_5)_2$ and give compounds which are converted on decarboxylation into dimethylene derivatives [96]:



Ethyl orthoformate adds on to ketene with the formation of ethyl diethoxypropionate [97]:

$$HC(OC_2H_5)_3 + CH_2 = CO \xrightarrow{BF_3} (C_2H_5O)_2CHCH_2COOC_2H_5$$

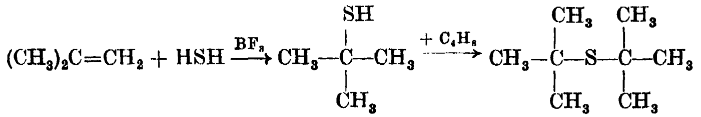
Dihydropyran with ethyl orthoformate in the presence of $BF_3 . O(C_2H_5)_2$ forms the 2-ethoxytetrahydropyran-3-carboxyaldehyde of diethylacetal [98].

5. REACTIONS OF ETHYLENIC COMPOUNDS WITH ORGANIC SUBSTANCES CONTAINING SULPHUR

The addition of mercaptans to olefines has been studied by many investigators. Posner [99] showed as early as 1905 that mercaptans are capable of being added to olefines, especially to such as trimethylethylene, styrene, α-methylstyrene, in the presence of acetic and sulphuric acids. It was later found that mercaptans and thioacetic acid add on to olefines against the Markownikoff rule. The reaction is accelerated by the presence of small quantities of peroxides.

Boron fluoride and its compounds have come into use quite recently as catalysts for the addition of hydrogen sulphide and mercaptans to olefines. When hydrogen sulphide acts on olefines in the presence of boron fluoride and its coordination compounds, mercaptans or sulphides (thioethers) are formed depending on the ratio of the reagents and other conditions.

Olefines of iso-structure with tertiary carbon atoms, and containing up to 24 carbon atoms in the molecule, for example *iso*butylene, di*iso*butylene, tri*iso*butylene and others, with hydrogen sulphide in the presence of BF_3 free and also as hydrates or coordination compounds with orthophosphoric acid, form the corresponding mercaptans in a 75—96 per cent yield [100—108]. It is recommended that the reaction be carried out at very low temperatures, for example from —70 to —30°. Thus, tri*iso*butylene and liquid H_2S in 1 : 2 ratio, saturated with 1·7 per cent BF_3 at a temperature of —30° gave a 78 per cent yield of mercaptans containing 96 per cent *tert.*-dodecylmercaptan [109]. *iso*Butylene with H_2S and BF_3 forms a mixture containing 4·3 per cent *tert.*-butylmercaptan and 66 per cent di-*tert.*-butyl sulphide. The reaction proceeds according to the Markownikoff rule and for *iso*butylene and hydrogen sulphide may be represented by the following scheme:



$$(CH_3)_2C{=}CH_2 + HSH \xrightarrow{BF_3} CH_3{-}\overset{\displaystyle SH}{\underset{\displaystyle CH_3}{C}}{-}CH_3 \xrightarrow{+\,C_4H_8} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}S{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3$$

Vinyl acetate with mercaptans in the presence of $BF_3 . O(C_2H_5)_2$ and HgO forms a 2-alkylmercaptoethyl acetate (I) with 75 per cent yield, but in the presence of $BF_3 . O(C_2H_5)_2$ without HgO gives it with 99 per cent yield, instead of the expected mercaptals (II) [13]:

$$CH_2{=}CHOCOCH_3 + R'SH \rightarrow \underset{(I)}{R'SCH_2CH_2OCOCH_3};\ \underset{(II)}{CH_3CH(SR')OCOCH_3}$$

Vinyl alkyl ethers add orthothio esters of formic acid in the presence of boron fluoride ethyl etherate with the formation of mixed acetalmercaptals [110]. Thus, vinyl methyl ether with ethyl *o*-thioformate in the presence of $BF_3 . O(C_2H_5)_2$ reacts according to the scheme

$$CH_2=CHOCH_3 + HC(SC_2H_5)_3 \rightarrow CH_3OCH(SC_2H_5)CH_2CH(SC_2H_5)_2$$

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CHAPTER VIII

THE ADDITION OF ORGANIC COMPOUNDS CONTAINING OXYGEN TO ACETYLENIC AND DIENIC HYDROCARBONS

At the present time interest in acetylenic and dienic compounds is exceptionally great. Among the numerous reactions, the catalytic addition of different reagents at the position of the unsaturated bonds attracts considerable attention. The investigations completed with boron fluoride used as a catalyst are considered below.

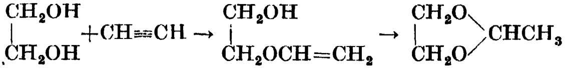
1. ADDITION OF WATER AND ALCOHOLS TO ACETYLENIC COMPOUNDS

On treatment with aqueous solutions of boron fluoride acetylene is easily converted into acetaldehyde [1]. Acetylene carbinols are hydrated by water in the presence of BF_3 to unsaturated ketones [2] according to the reaction

$$(CH_3)_2(COH)C{\equiv}CH \xrightarrow[BF_3]{+H_2O} (CH_3)_2C(OH)COCH_3 \xrightarrow{-H_2O} CH_2{=}C(CH_3)COCH_3$$

Acetylene and its homologues, like olefines, add on alcohols in the presence of BF_3 and its coordination compounds. But since these hydrocarbons have a triple bond, two molecules of alcohol are usually added.

All monohydric aliphatic alcohols add on to acetylene in such a way that alkylvinyl ethers are first formed, and these in an acid medium add a second molecule of alcohol according to the Markownikoff rule and form acetals [3]. Dihydric alcohols with acetylene in the presence of BF_3 are converted into cyclic acetals [4]:



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + CH{\equiv}CH \rightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OCH{=}CH_2 \end{matrix} \rightarrow \begin{matrix} CH_2O \\ | \\ CH_2O \end{matrix}\!\!>CHCH_3$$

Glycol monoalkyl ethers with acetylene form acetals of the glycol monoethers [5]. Methyl and *iso*butyl glycollates add to acetylene in the presence of $BF_3 \cdot CH_3OH$ and HgO with the formation of acetals of bishydroxyacetates of the general formula $CH_3CH(OCH_2COOR)_2$ with a yield of 81 and 70 per cent respectively [6, 7]. Glycerol with acetylene at a temperature below 100° forms acetals of glycerol [8].

The addition of *cyclo*hexanol to acetylene in the presence of BF_3 proceeds with difficulty and is accompanied by resin formation [9]. Furfuryl alcohol undergoes decomposition when it reacts with acetylene, but tetrahydrofurfuryl alcohol is easily added on in the presence of BF_3 [9]. Amino-alcohols do not add on to acetylene, which is explained by the deactivating action of the amino group of these alcohols on the catalytic activity of boron fluoride.

Monoalkylacetylenes add on alcohol in the presence of $BF_3 . CH_3OH$ and HgO with the formation of the corresponding ketals [10]. Methyl-, ethyl-, propyl-, butyl- and amyl-acetylenes most readily add on methyl alcohol. The higher *n*-alcohols add on to the specified alkylacetylenes very vigorously in the presence of BF_3 and HgO. but polymeric products are also formed and the ketals cannot be separated [11]. If a little trichloracetic acid (0·2—1 g per mole of alkylacetylene) is added to the BF_3 and HgO catalyst, the reaction proceeds quietly with high yields of 2,2-dialkoxyalkanes [12]. Alcohols of iso-structure in the same conditions either do not react at all or add on, but with great difficulty.

Polyhydric alcohols (glycol, glycerol, chlorohydrin and others) add on to alkylacetylenes and form dioxolanes [13].

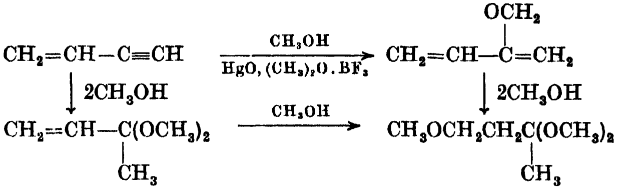
A particular position among substituted acetylenes is occupied by monovinylacetylene in which the double and triple bonds capable of addition reactions are found in a conjugated position. According to the results of Carothers and collaborators [14], monovinylacetylene in the presence of sodium methylate adds on one molecule of methyl alcohol in the 1,4 position and by the subsequent isomerization of the product formed gives methoxybutyne.

Rotenberg and Favorskaya [15] studied this reaction in the presence of BF_3 and HgO and found that monovinylacetylene reacts differently with methyl and ethyl alcohols. Ethyl alcohol adds on at the triple bond and forms ethoxy-2-butadiene-1,3. A molecule of methyl alcohol also first adds on at the triple bond, but then the methoxy-2-butadiene-1,3 formed splits off a molecule of methyl alcohol and adds it on again in the 1,2 position with the formation of methoxy-2-butadiene-2,3.

If, however, a mixture of BF_3, HgO and CCl_3COOH is used as catalyst in the specified reaction, the monovinylacetylene adds on three molecules of methyl alcohol and forms 2,2,4-trimethoxybutane [16, 17].

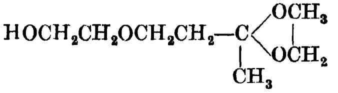
Vinylethylacetylene, like monovinylacetylene, adds on three molecules of methyl alcohol in the presence of BF_3, HgO and CCl_3COOH, but alkylallylacetylenes, like 4-methoxy-2-butyne, add on two molecules of methyl alcohol at the triple bond only [18, 19].

All these investigations show that the addition of methyl alcohol to monovinylacetylene takes place first at the triple bond [20], but then according to the following scheme:



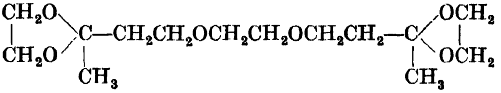
$$\begin{tikzcd} CH_2{=}CH{-}C{\equiv}CH \arrow[r, "CH_3OH", "HgO,\,(CH_3)_2O.BF_3"'] \arrow[d, "2CH_3OH"] & CH_2{=}CH{-}\overset{\displaystyle OCH_2}{\overset{|}{C}}{=}CH_2 \arrow[d, "2CH_3OH"] \\ CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OCH_3)_2 \arrow[r, "CH_3OH"] & CH_3OCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}(OCH_3)_2 \end{tikzcd}$$

Higher alcohols also add three molecules to monovinylacetylene according to the same scheme [21]. Monovinylacetylene and ethylene glycol in the presence of $BF_3 . O(C_2H_5)_2$, HgO and CCl_3COOH form two addition products of the following structure:



$$HOCH_2CH_2OCH_2CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}\begin{matrix} \diagup OCH_3 \\ | \\ \diagdown OCH_2 \end{matrix}$$

and



$$\begin{matrix} CH_2O\diagdown \\ | \\ CH_2O\diagup \end{matrix}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2CH_2OCH_2CH_2OCH_2CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}\begin{matrix} \diagup OCH_2 \\ | \\ \diagdown OCH_2 \end{matrix}$$

Other polyhydric alcohols, for example glycerol chlorohydrin and mannitol, also react in a similar way.

Nieuwland and collaborators [19] did not succeed in establishing the addition of methyl alcohol to divinylacetylene in the presence of BF_3 and HgO on account of the strong polymerization of the hydrocarbon. A. L. Klebanskii and collaborators [22] considered it probable that divinylacetylene in the presence of $BF_3. O(C_2H_5)_2$ and HgO adds one molecule of methyl alcohol and forms 3-methoxyhexatriene-1,3,4.

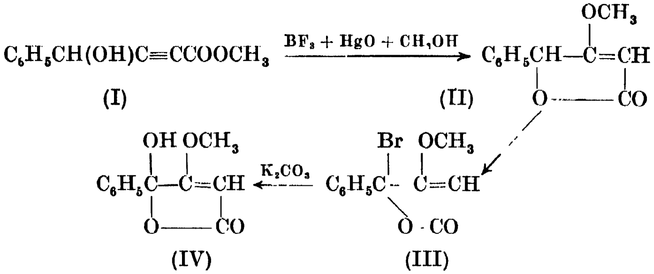
In recent years much attention has been paid to the study of the reaction of acetylenic carbinols with aliphatic alcohols.

First I. N. Nazarov [23, 24] and almost simultaneously Hennion *et al.* [25] studied the reaction of alcohols with dialkylethinyl carbinols in the presence of BF_3 and HgO and found that alcohols from methyl to *n*-amyl inclusive add at the triple bond of the carbinol with the formation of ketals of dialkylacetyl carbinols with 60—80 per cent yield and of dialkoxyhexaalkyldioxanes with a yield of 10—15 per cent. The main reaction here may be represented by the equation

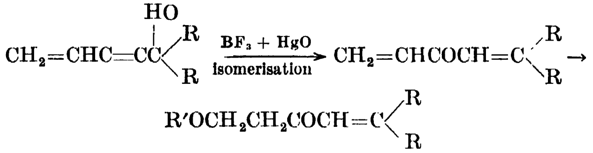
$$(CH_3)_2C(OH)C \equiv CH + 2ROH \rightarrow (CH_3)_2C(OH)C(OR)_2CH_3$$

Glycol adds to dimethylethinylcarbinol to the extent of one molecule and forms a cyclic ketal [26].

Methyl phenylhydroxytetrolate (I) with methyl alcohol in the presence of a catalyst prepared from $BF_3 . O(C_2H_5)_2$, HgO, CH_3OH and CCl_3COOH, forms a methoxylactone (II), by the bromination of which and subsequent hydrolysis with potash in aqueous dioxane an analogue of penicillinic acid (IV) is obtained [27]. The whole conversion may be represented by the following scheme:



Tertiary vinylethinyl carbinols in reaction with alcohols in the presence of BF_3 and HgO are first isomerized to β,β-dialkyldivinyl ketones, and the latter then add on one molecule of alcohol at the double bond of the vinyl [28, 29] according to the scheme



$$CH_2{=}CHC{\equiv}C\overset{HO}{C}\!\begin{smallmatrix}R\\R\end{smallmatrix} \xrightarrow[\text{isomerisation}]{BF_3 + HgO} CH_2{=}CHCOCH{=}C\!\begin{smallmatrix}R\\R\end{smallmatrix} \rightarrow$$
$$R'OCH_2CH_2COCH{=}C\!\begin{smallmatrix}R\\R\end{smallmatrix}$$

Secondary vinylethinyl carbinols add two molecules of methyl alcohol and form the corresponding dimethoxyketones [30].

At present there is not one investigation or item of patent information on the use of BF_3 and its coordination compounds for the addition of hydrogen sulphide and mercaptans to acetylenic hydrocarbons. This reaction, as seen from the review of I. L. Knunyants and A. V. Fokin [31], has been studied with a number of other catalysts. It cannot be doubted that in the given reaction BF_3 will possess a high catalytic activity owing to its capacity of forming highly active complexes with thiocompounds.

2. ADDITION OF ALCOHOLS TO DIENIC HYDROCARBONS

Boron fluoride has been used as a catalyst in the addition of alcohols to dienic hydrocarbons since 1946. Of acyclic hydrocarbons only the reaction of hexadiene-1,2 with methyl alcohol in the presence of the catalyst $BF_3 . O(C_2H_5)_2{-}HgO{-}CH_3OH$ has been investigated, as a result of which 2,2-dimethoxyhexane is obtained [32]. The addition of alcohols to cyclic dienic hydrocarbons has been better studied.

*cyclo*Pentadiene with allyl alcohol and $BF_3 \cdot O(C_2H_5)_2$ forms 2,5-endomethylene-1,2,5,6-tetrahydrobenzyl alcohol, which easily undergoes cyclization [33].

Di*cyclo*pentadiene with monohydric saturated [34] and unsaturated [35] alcohols, with nitroalcohols [36], polyhydric alcohols [37, 38], thiocyanoalcohols [39] and ethero- or haloalcohols [40, 41] in the presence of boron fluoride etherates reacts in such a way that at the position of one double bond it adds on a molecule of alcohol, and as a result the corresponding ethers of dihydro*cyclo*pentadiene are formed.

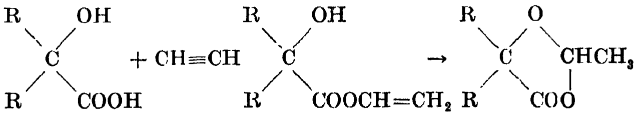
The condensation products of *cyclo*pentadiene with unsaturated compounds [42—44], for example 1,4-endomethylenetetrahydrofluorene obtained by the condensation of *cyclo*pentadiene with indene, also add on one molecule of alcohol, halohydrin or thiocyanic alcohol in the presence of BF_3 and its compounds.

Similarly alcohols and their derivatives react with polycyclopentadienes which have two double bonds [45].

3. ADDITION OF CARBOXYLIC ACIDS AND CHLOROANHYDRIDES TO ACETYLENIC AND DIENIC COMPOUNDS

The addition of organic acids at the triple bond, in contrast to the reaction with olefines, passed the laboratory method of investigations long ago and is now carried out on an industrial scale.

The beginning of the use of boron fluoride as a catalyst for this reaction dates from 1938. According to the results of Yu. S. Zalkind *et al.* [46], acetylene with formic acid in the presence of BF_3 and HgO at a temperature of 30—35° forms vinyl formate with a yield of 66·7 per cent. Vinyl acetate is obtained from acetylene and acetic acid in the presence of BF_3 and HgO with a yield of 80—85 per cent [47—49]. Butyric, crotonic [50] and higher monobasic acids [51] also add to acetylene in the presence of BF_3 and its compounds and form vinyl esters with high yield. With acetylene, hydroxy acids are converted into vinyl esters or secondary products of the reaction — the acetals of hydroxyacids [4] according to the scheme

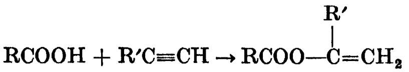


When dry acetylene is passed into lactic acid in the presence of a boron fluoride coordination compound with acetic acid and HgO vinyl lactate is obtained [52].

Partial alkyl [53] or alkenyl [54] oxalates, malonates or succinates add on to acetylene in the presence of the specified catalysts with the formation of vinylalkyl or vinyl alkenyl esters.

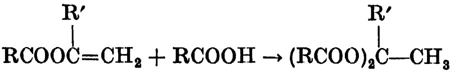
The reaction of alkylacetylenes with organic acids had already been studied by Behal and Desgrez in the last century [55] by heating the reagents in sealed tubes at a temperature of 250—280°. But the authors did not succeed in separating the addition products. Nieuwland *et al.* [56] found that monobasic aliphatic acids with monoalkylacetylenes in the presence of a BF_3 and HgO catalyst react with the formation of α-alkylvinyl esters of carboxylic acids and by-products, ketones :

(I)



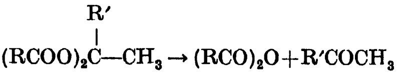
$$RCOOH + R'C{\equiv}CH \rightarrow RCOO{-}\overset{R'}{\overset{|}{C}}{=}CH_2$$

(II)



$$RCOO\overset{R'}{\overset{|}{C}}{=}CH_2 + RCOOH \rightarrow (RCOO)_2\overset{R'}{\overset{|}{C}}{-}CH_3$$

(III)



$$(RCOO)_2\overset{R'}{\overset{|}{C}}{-}CH_3 \rightarrow (RCO)_2O + R'COCH_3$$

When methylacetylene was reacted with acetic acid in the presence of BF_3 in ether solution *iso*propenyl acetate was obtained.

A. D. Petrov and V. D. Azatyan [57] studied the reaction of mono and dialkylacetylenes with acrylic, crotonic, undecylene and oleic acids in the presence of BF_3 and HgO and found that in the conditions used by Nieuwland, the acids enumerated do not form esters according to scheme (I), but are converted into ketones, which the authors explain by the small stability of the alkylvinyl esters of these acids.

The reaction of monovinylacetylene with organic acids is of considerable interest. By analogy with the reaction of monovinylacetylene with alcohols, the addition of three molecules of acid to the monovinylacetylene molecule had to be expected. But in reality monovinylacetylene in the presence of BF_3 and HgO or $BF_3 . O(C_2H_5)_2$ adds only one molecule of acid and forms analogues of *iso*prene [58].

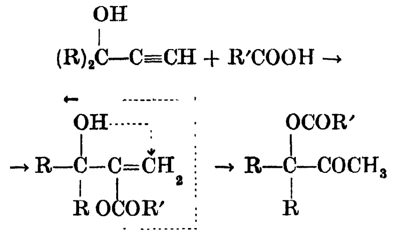
A L. Klebanskii and K. K. Chevychalova [59] investigated the addition of formic and acetic acids to monovinylacetylene in the presence of different catalysts ($ZnSO_4$, $ZnCl_2$, ZnO, CaO, CuO, etc.) and found that only the BF_3 and HgO catalyst deserved attention, because it enabled 1,3-butadiene-2-formate to be obtained with a yield of 21 per cent and and 1,3-butadiene-2-acetate with a yield of more than 30 per cent. [60].

There are indications that the reaction of acetylene with acids in the presence of BF_3 may be directed in such a way that vinylmethyl ketone and the anhydride of the acid will be obtained with 80 per cent yield [61].

Not devoid of interest is information about the use of BF_3 for the addition of liquid HF to acetylene in an improved method of preparing ethylidene fluoride [62].

Dimethyl- and diethyl-ethinyl carbinols add on one molecule of organic acid (formic, acetic, propionic and butyric) in the presence of $BF_3O(C_2H_5)_2$ and HgO and form esters of dialkylacetylcarbinol [24, 63].

The most probable mechanism of the reaction in the opinion of I. N. Nazarov [24] is the addition of a molecule of acid to the carbinols at the triple bond with the formation of vinyl esters and the conversion of the latter to acyl esters by direct isomerization or intramolecular alcoholysis. The process, including the isomerization reaction may be represented by the scheme



$$(R)_2\overset{\displaystyle OH}{\overset{|}{C}}{-}C{\equiv}CH + R'COOH \rightarrow$$

$$\rightarrow R{-}\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}{-}\underset{\displaystyle OCOR'}{\underset{|}{C}}{=}CH_2 \rightarrow R{-}\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle OCOR'}{\overset{|}{C}}}}{-}COCH_3$$

If, however, dimethylethinylcarbinol is boiled for a prolonged period with formic acid, instead of the expected ester a dehydration product, methylvinylacetylene, is obtained with a yield of 74 per cent [64].

Acetylenic γ-glycols, for example 2,5-dimethyl-3-hexyne-2,5-diol, may add one or two molecules of acetic acid at the triple bond in the presence of BF_3 and form the corresponding acetates [65].

Thioacids with acetylene and its homologues [66], depending on the ratios of the reagents, give compounds of two types:

$$RCH = CHSCOR' \quad \text{and} \quad RCH(SCOR')CH_2SCOR'$$

On the addition of organic acids to divinyl there is the preliminary information of A. A. Petrov [67], according to which divinyl adds one molecule of acetic acid in the presence of mercury salts and forms methylvinylcarbinol acetate with a very small yield. S. V. Zavgorodnii [68] studied the addition of organic acids to divinyl in the presence of boron fluoride ethyl etherate and found that divinyl adds organic acids in the quantity of one molecule in the 1,2 position according to the scheme

$$CH_2 = CHCH = CH_2 + RCOOH \rightarrow CH_2 = CHCH(CH_3)OCOR$$

However, the addition reaction in the presence of $BF_3 \,.\, O(C_2H_5)_2$ proceeds very slowly and is accompanied by polymerization of the divinyl, and moreover the divinyl polymerizes more vigorously the stronger the acid. Thus, when formic and acetic acids are heated on a boiling water bath with divinyl in the presence of $BF_3 . O(C_2H_5)_2$ methylvinylcarbinol esters are formed with a yield of about 3 per cent. But meanwhile the divinyl hardly polymerizes at all. This is also observed with bromoacetic acid. When heated on a boiling water bath for 2 hr with chloroacetic acid and $BF_3 . O(C_2H_5)_2$, divinyl is quantitatively converted into a tough, solid rubber. In the case of trichloroacetic acid, divinyl is vigrously polymerized to a tough, solid rubber even at room temperature.

4-Vinyl*cyclo*hexene with chloroacetic acid in the presence of $BF_3 . O(C_2H_5)_2$ in chloroform solution forms a mixture of vinyl*cyclo*hexene mono- and dichloroacetates with 30·6 and 25 per cent yield respectively [69]. The reaction is accompanied by polymerization.

With thioglycollic acid chloroprene and its polymers form addition products of the general formula $(C_4H_6Cl)_n . SCH_2COOH$ (n from 2 to 12) [70].

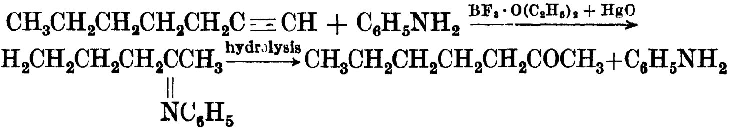
There are indications that divinylsulphone adds two molecules of *o*-mercaptobenzoic acid at the mercapto groups [71]. Divinyl with HCN in the presence of boron fluoride gives unsaturated polynitriles [72], but with colophony forms esters [73].

The polymerization products of *cyclo*pentadiene—di*cyclo*pentadiene and tri*cyclo*pentadiene — in the presence of BF_3 and its etherates add one molecule of organic or mineral acid [74—81].

Acetylenic hydrocarbons add to chloroanhydrides of aliphatic acids in the presence of BF_3 and form β-chlorovinylalkyl ketones [82]. When heated to 210° at a pressure of 30 atm with sulphur trioxide and BF_3 monovinylacetylene is converted into a brownish-yellow powder which is stable to heat [83].

4. ADDITIONS OF ARYLAMINES TO ACETYLENIC HYDROCARBONS

Amino alcohols, as mentioned above, do not react with acetylene in the presence of BF_3. In contrast to this, aromatic and aliphatic—aromatic amines react comparatively easily with acetylenic hydrocarbons. Acetylene adds on aniline in the presence of BF_3 and mercury or copper salts with the formation of ethylideneaniline [84, 85]. Heptyne with aniline forms as the main product an anil, which hydrolyses into methyl amyl ketone and aniline [86]:



$$CH_3CH_2CH_2CH_2CH_2C\equiv CH + C_6H_5NH_2 \xrightarrow{BF_3\cdot O(C_2H_5)_2 + HgO}$$

$$\rightarrow CH_3CH_2CH_2CH_2CH_2\underset{\underset{NC_6H_5}{\|}}{C}CH_3 \xrightarrow{\text{hydrolysis}} CH_3CH_2CH_2CH_2CH_2COCH_3+C_6H_5NH_2$$

A dark yellow oil of unsaturated character is obtained as a side product, which is evidently an addition product of one molecule of aniline to two molecules of heptyne. Secondary amines, such as diethylamine, and heptyne form an N-disubstituted heptylenamine, which is converted on hydrolysis into methylamyl ketone and diethylamine [86]. Diethylaniline does not react with heptyne-1 in the conditions studied, because this amine has no active hydrogen atoms on the nitrogen [86].

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CHAPTER IX

ISOMERIZATION AND CYCLIZATION REACTIONS

1. ISOMERIZATION OF HYDROCARBONS

THE isomerization of feebly reactive low molecular paraffins of normal structure to isoparaffins is at present widely carried out in industry in the presence of many catalysts. Boron fluoride has been used since about 1940 as a catalyst or as an activator of halogen compounds of aluminium and of hydrofluoric acid for this reaction.

The isomerization of paraffins to isoparaffins is invariably accompanied by the more deep-seated disproportionation of the hydrocarbons, i. e. by their resolution into lower and higher ones. Therefore besides the isoparaffins with the same number of carbon atoms as the original paraffins, a small amount of hydrocarbons is formed with a smaller or greater number of carbon atoms in the molecules.

The isomerization of *n*-butane to *iso*butane is particularly important from a practical point of view. In the presence of boron fluoride or its compounds with water, hydrofluoric acid, aluminium chloride or bromide and other compounds it may be brought about both in the liquid and in the vapour phases at a temperature from 100 to 270° and a pressure of 20—80 atm [1—16].

For the liquid phase isomerization of *n*-butane to *iso*butane a liquid catalyst, prepared by saturating water with gaseous boron fluoride at a temperature of 100—120° to the composition $BF_3 . H_2O$, is recommended [4]. Instead of water 50 per cent HF may be used. There are indications that below 80° *n*-butane is not isomerized in the presence of the catalyst $BF_3 . H_2O$ [2].

Vapour phase isomerization in the presence of a mixed catalyst Al_2O_3—$AlCl_3$—BF_3 is known [12].

The higher *n*-paraffins (pentane, hexane, etc.) are also isomerized to hydrocarbons of iso-structure in the presence of boron fluoride and its compounds [17—34]. Thus, 380 g pentane, 100 g HF and 100 g BF_3 at a temperature of 150° and increased pressure in the course of 60 min form liquid products which contain 20 per cent by weight of *iso*pentanes. In the presence of 1 per cent benzene, other conditions being equal the liquid products comprising 73 per cent contain 41 per cent *iso*pentanes [27]. In a similar way *n*-heptane in the presence of BF_3 and HF isomerizes with the formation of a number of isoparaffins [29].

C_7 isoparaffins, for example methyl hexanes and dimethylpentanes, in the presence of BF_3 and HF in propane are converted into 2,2,3-tri-methyl butane or triptane [28]. But in this case, disproportionation [35] readily takes place in addition to isomerization and a mixture of isoparaffins of lower and higher molecular weight (in relation to the original hydrocarbons) is obtained.

Data about the isomerization and disproportionation of certain paraffins in the presence of BF_3 and HF are given in Table 76.

The isomerization of paraffins is facilitated by the presence of naphthenic or aromatic hydrocarbons. For example, a mixture of hexane (68·7 g), methyl*cyclo*pentane (8·3 g), HF (116 g) and BF_3 (37 g), heated for 1 hr at 176°, gives *iso*butane 0·7 per cent, *iso*pentane 1·64 per cent, 2,2-dimethylbutane 5·63 per cent, 2,3-dimethylbutane 1·18 per cent, methylpentane 45·43 per cent, *n*-hexane 38·04 per cent and *cyclo*hexane 7·38 per cent [20]. Pentane with an equimolecular quantity of HF and 2·6—3·1 per cent boron fluoride in the presence of small quantities of benzene at a temperature of 76—90° isomerizes to 2-methylbutane with a 54·7 per cent yield [21]. Hexane with HF and 2·1—7 per cent BF_3 at temperatures 140—176° and increased pressure isomerizes to 2,2- and 2,3-dimethylbutanes [23].

Combining isomerization with hydroforming of gasolines in the presence of BF_3, a high octane motor fuel of the neohexane type is obtained [22].

For the isomerization of hexane and higher paraffins it is recommended that

Table 76. Isomerization and disproportionation of paraffins in the presence of $BF_3 + HF$

Original hydrocarbon	Conditions of reaction		Compounds formed (%)											Literature reference
	Temp. (°C)	Time	C_3H_8	*iso*-C_4H_{10}	*n*-C_4H_{10}	*iso*-C_5H_{12}	*n*-C_5H_{12}	2,2-dimethyl butane	di-*iso*-propyl	2-methyl pentane	3-methyl pentane	*n*-C_6H_{14}	Higher hydrocarbons	
C_3H_8	82·5	2 hr	11·7	87·0	—	—	—	—	—	—	—	—	—	[5]
n-C_5H_{12}	73—165		2·1	36·1	9·9	20·9	5·8	—	—	—	—	—	25·2	[11]
n-C_6H_{14}	180	40 min	—	—	0·5	—	0·6	6·5	7·9	24·9	10·5	41·5	7·6	[11]
n-C_6H_{14}	260	35 min	13·8	27·6	9·0	18·1	4·5	—	—	—	—	3·9	14·5	[11]

fluorohydrocarbons such as C_7F_{16}, $C_6F_{12}Cl_2$, $C_7F_{12}H_4$, $C_7H_{12}F_2Cl_2$ [26] be used as solvents.

The gas oil and lubricating oil fractions from the cracking of petroleum may undergo isomerization in the presence of BF_3 [36].

Besides BF_3 and HF, Al_2O_3 with precipitated SiO_2 (5—10 per cent) treated with boron fluoride [19], and BF_3 with SO_3HF [25], are recommended as catalysts for the isomerization of paraffins.

Naphthenic hydrocarbons in the presence of BF_3 and HCl or HF, depending on the conditions, are converted into isoparaffinic or into *cyclo*hexane hydrocarbons [37]. Thus naphthenic hydrocarbons are converted into isoparaffins [37] with hydrogen and an HF + BF_3 catalyst (1—40 per cent) at a temperature of 150—450° and increased pressure, and compounds such as methyl*cyclo*pentane isomerize to *cyclo*hexane [20]. Thus the conversion consists in the breaking and enlargement of the rings.

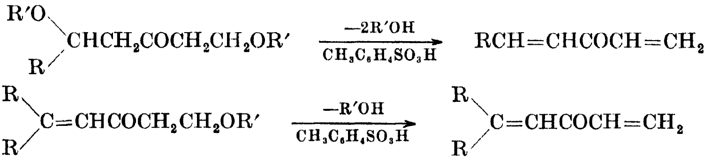
Aliphatic and cyclic olefines can undergo isomerization in the presence of boron fluoride etherates [38].

Under the influence of BF_3 at a temperature of 300—600° and increased pressure hydronaphthalenes are converted into products suitable as solvents for lacquers [39].

o- and *p*-Xylenes in the presence of BF_3 and HF at a temperature of 175—225° isomerize into *m*-xylene [40].

2. ISOMERIZATION OF VINYLETHINYLCARBINOLS

In the presence of BF_3 and red mercuric oxide vinylethinylcarbinols of the general formula $RCH(OH)C{\equiv}C{-}CH{=}CH_2$ isomerize to substituted divinyl ketones [41], which are very reactive compounds, and if the isomerization is carried out in alcoholic solutions they are not usually separated as final products because they react readily with alcohols and are converted into mono- and dialkoxyketones, as indicated in Chap. VII. But if these alkoxyketones are subjected to distillation in a low vacuum in the presence of *p*-toluene sulphonic acid, divinyl ketones may be obtained in the free state. The conversion may be represented by the following reactions:



$$\begin{matrix}R'O\\R\end{matrix}\!\!>CHCH_2COCH_2CH_2OR' \xrightarrow[CH_3C_6H_4SO_3H]{-2R'OH} RCH{=}CHCOCH{=}CH_2$$

$$\begin{matrix}R\\R\end{matrix}\!\!>C{=}CHCOCH_2CH_2OR' \xrightarrow[CH_3C_6H_4SO_3H]{-R'OH} \begin{matrix}R\\R\end{matrix}\!\!>C{=}CHCOCH{=}CH_2$$

In this way, the isomerization of vinylethyl carbinols may be regarded as a simple, quite practicable method of preparing divinyl ketones.

Unsaturated glyceridic oils, heated with boron fluoride for 1—2 hr at a temperature of 450—600°, undergo structural isomerization [42]. Tri- and tetraacetylglucosides isomerize in the presence of free boron fluoride [43, 44]. Methyl-2,3,4-triacetyl-β-D-xyloside with m. p. 114·5—115·5°, saturated with BF_3 in chloroform is converted into methyl-2,3,4-triacetyl-α-D-xyloside with m. p. 86—87°.

In studying the reaction of α-oxides with alcohols A. A. Petrov [45] observed the isomerization of *iso*butylene oxide to *iso*butyraldehyde in the presence of boron fluoride ethyl etherate.

B. A. Arbuzov and collaborators [46] investigated the isomerization of the oxide of the nitrile of 2,5-dimethyl-Δ^3-*cyclo*hexene carboxylic acid, 5,8,9,10-tetrahydronaphthoquinone-1,4 oxide and 1,4,5,8,11,12,13,14-octahydroanthraquinone dioxide in the presence of boron fluoride ethyl etherate, but in no case were definite isomerization products separated.

3. ISOMERIZATION OF ALKYLPHENYL ETHERS

The isomerization of these ethers to alkylphenols has been studied by many research workers in the presence of different catalysts. At the present time it is almost universally recognized that when phenols are reacted with olefines, alcohols, ethers or alkyl halides in the presence of acid catalysts in comparatively mild conditions, alkylphenyl ethers are first formed, which then isomerize to alkylphenols. The ease and order of the isomerization reaction depends on the temperature, time, catalyst, size and structure of the alkyl radical and on the presence of substituents in the benzene ring.

Boron fluoride is a very strong isomerizing agent. It can isomerize even such ethers as anisole, which are stable to isomerization. It has been found, for example, that on heating a mixture of phenol and boron fluoride methyl etherate to boiling, methylation of the benzene ring takes place through the formation of anisole and its isomerization to cresols [47].

It was demonstrated by S. V. Zavgorodnii [48—50] that the alkylation of phenols with pseudobutylene, pentene-2 and *cyclo*hexene in the presence of 5—10 per cent $BF_3 \cdot O(C_2H_5)_2$ took place through the formation of alkylphenyl ethers as intermediate products, which isomerized to alkylphenols. He also showed that *o*-chlorophenol *cyclo*hexyl ether does not undergo isomerization even when heated with 25 per cent $BF_3 \cdot O(C_2H_5)_2$ to 120—140° for 8 hr.

Phenol is alkylated with propylene in the presence of boron fluoride through the formation of *iso*propylphenyl ethers and their isomerization to *iso*propyl phenols [51].

When gaseous boron fluoride is passed into pure *iso*propylphenyl ether at room temperature it undergoes complete conversion in the course of a few minutes with the evolution of a considerable amount of heat [52]. In addition there is formed a mixture of phenolic and ethereal products of the same composition as in the alkylation of phenol with propylene in the presence of BF_3. For example, from 250 g *iso*propylphenyl ether there is obtained (in g): phenol 90; 2-*iso*propylphenol 34; 2,4-di*iso*propylphenol 44; 2,4,6-tri*iso*propylphenol 28; traces of phenyl*iso*propyl and 2-*iso*propylphenyl*iso*propyl ethers; 2,4-di*iso*propylphenyl*iso*propyl ether 32; 2,4,6-tri*iso*propylphenyl*iso*propyl ether 12.

In the given case, intramolecular and intermolecular isomerization of the ethers probably takes place simultaneously, and direct propylation of the *iso*propylphenyl ethers in such a way that an *iso*propyl group is transferred from the ether oxygen of one molecule to the phenolic oxygen of another molecule, and also from the oxygen atom to a carbon atom of the ring within the ether molecule.

The *iso*propyl ether of 4-methylphenol undergoes a similar conversion in the presence of BF_3 with the formation of a mixture of phenolic and ethereal compounds, viz.: 4-methylphenol; 4-methyl-2-*iso*propyl phenol; 4-methyl-2,6-di*iso*propylphenol; 4-methyl-2-*iso*propylphenyl*iso*propyl ether and 4-methyl-2,6-di*iso*propylphenyl*iso*propyl ether [52]. When gaseous BF_3 is passed into the *iso*propyl ether of 2-methylphenol and the mixture is heated for a few minutes at 85° it isomerizes mainly to 2-methyl-4-*iso*propylphenol. More highly substituted phenolic and ethereal compounds are formed in small quantities. 3-Methylphenol *iso*propyl ether (98 g) with boron fluoride (3 g) in the same conditions forms 63 g or 64 per cent of the theoretical yield of the following conversion products: thymol, 3-methyl-4-*iso*propyl phenol, 3-methyl-4,6-di*iso*propyl phenol and 3-methyl-4,6-di*iso*propylphenyl ether [53].

In certain conditions *o*-alkylphenols may be converted into *p*-alkylphenols [54] under the influence of boron fluoride, and *p*-alkylphenols into *o*-alkylphenols [55].

*cyclo*Hexyl ethers of phenol and cresols with BF_3 undergo isomerization to the corresponding derivatives [56].

When *iso*bornylphenyl ether (200 g) in benzene solution (300 ml), in the presence of 2 g $BF_3 . O(C_2H_5)_2$, is heated under reflux condenser for 7 hr, it gives mono*iso*bornyl phenol (53 g), di*iso*bornyl phenol (39 g) and tri*iso*bornyl phenol (30 g) [57]. 4-Methylphenol*iso*bornyl ether isomerizes mainly to 2,6-di*iso*bornyl-4-methylphenol, but *iso*bornyl-2,4-xylyl ether by the same method is converted to the extent of 87 per cent into 6-*iso*bornyl-2,4-dimethylphenol [57].

Isomerization of Alkyl Esters of Aromatic Hydroxyacids

All three (*o*-, *m*- and *p*-) hydroxybenzoic acids are alkylated by propylene in the presence of BF_3 with the formation of esters of hydroxybenzoic acids as intermediate products. But the isomerization of their esters proceeds differently. The *iso*propyl group of esters of salicylic acid and to a considerable extent of *m*-hydroxybenzoic acid migrates under the influence of boron fluoride from the ether oxygen of the carboxyl to the aromatic ring with the formation of *iso*propylhydroxybenzoic acids [58]. The *iso*propyl group of the *p*-hydroxybenzoic ester first migrates from the ether oxygen of the carboxyl group to the oxygen of the hydroxyl group, forming *iso*propoxybenzoic acid, and then it migrates to the benzene ring [59].

When *n*-propyl salicylate is heated to 130—140° in the presence of BF_3 for 2 hr, it isomerizes with the formation of 2-hydroxy-3-*iso*propyl-, 2-hydroxy-5-*iso*propyl- and 2-hydroxy-3,5-di*iso*propylbenzoic acids [60].

n-Butyl salicylate is converted with BF_3 into *sec.*-butylsalicylic acids with a predominance of the *o*-substituted ones, but *iso*butyl salicylate isomerizes almost quantitatively to *p*-*tert.*-butylsalicylic acid.

The alkylation of salicylic acid with higher olefines [61], and also with *iso*propyl, *sec.*-and *tert.*-butyl alcohols [60] takes place via the isomerization of the alkyl esters originally formed.

The isomerization of alkyl esters of aromatic hydroxyacids is of definite interest because the decarboxylation of the alkoxycarboxylic acids formed on isomerization is a convenient method of preparing pure alkylphenols.

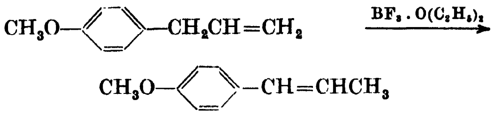
Isomerization of Alkenylphenolic Ethers

Alkenylphenolic ethers are often capable of isomerization on heating even in the absence of catalysts. The presence of a boron fluoride catalyst considerably facilitates the isomerization and enables it to be carried out in milder conditions.

L. Ya. Bryusova and M. L. Ioffe [62] studied the isomerization of the allyl ether of guaiacol and showed that if it is carried out in the presence of a $BF_3 . 2CH_3COOH$ catalyst, the allyl radical migrates mainly to the *p*-position, in spite of the presence of a free *o*-position in the ether molecule.

Making use of the property of allylphenolic ethers in certain conditions of undergoing *p*-isomerization in the presence of a free *o*-position, Bryusova and Ioffe worked out a simple and convenient synthesis of the valuable perfume eugenol by means of the isomerization described above, with a yield of eugenol of about 38 per cent. However, in the given case, as in the isomerization of alkylphenolic ethers, other products (guaiacol, eugenol allyl ether, etc.) are formed besides the main product of isomerization, eugenol.

Under the influence of boron fluoride isomerization processes take place which are connected only with the migration of the double bond and the hydrogen atom in the allyl residue. It is known, for example, that methylchavicol if left with $BF_3 . O(C_2H_5)_2$ for 48 hr at room temperature, isomerizes to metanethole [63]. The regrouping may be represented by the equation

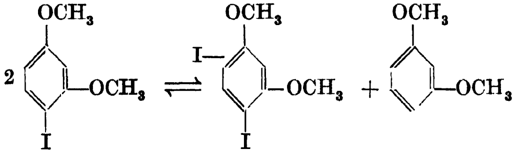


Interesting regroupings of phenolic ethers of aliphatic carboxylic acids in the presence of boron fluoride, the so-called Fries rearrangements, are described in Chap. XI.

4. REARRANGEMENTS CONNECTED WITH THE MIGRATION OF THE HALOGEN ATOM IN THE BENZENE RING

The migration of the aromatically linked halogen in certain ethers of polyhydric phenols in the presence of boron fluoride deserves attention.

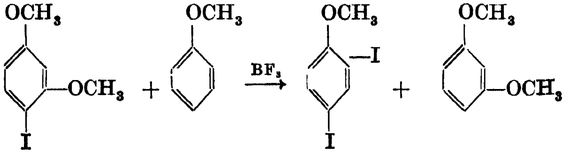
Meerwein and collaborators [64] found that 4-iodoresorcinol dimethyl ether (I) is converted under the influence of $BF_3 . O(C_2H_5)_2$ into 4,6-diiodoresorcinol dimethyl ether (II) and resorcinol dimethyl ether (III), which are found in equilibrium with the original ether:



(I) (II) (III)

The reversibility of the given reaction is confirmed by the fact that when a solution of the compounds (II) and (III) in CH_3COOH is heated to 120° the first can be obtained with a yield of 88 per cent.

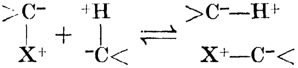
The migration of the iodine may therefore be considered as an intermolecular iodination which is brought about between two molecules of 4-iodoresorcinol dimethyl ether. This conclusion is confirmed by the iodination of anisole with 4-iodoresorcinol dimethyl ether to *p*- and *o*-iodoanisole according to the following equation:



The colourless reaction mixture from beginning to end of the reaction and the inability of resorcinol dimethyl ether of being iodinated with elementary iodine in the presence of $BF_3 . O(C_2H_5)_2$ proves that the iodine atom, which migrates from one benzene ring to the other, is never in an absolutely free state.

In the presence of BF_3 or $BF_3 . O(C_2H_5)_2$, 4-bromoresorcinol dimethyl ether, like the iodine derivative, is converted into 4,6-dibromoresorcinol dimethyl ether and resorcinol dimethyl ether. But the migration of bromine in this reaction takes place much more slowly than that of iodine. The chlorine atom migrates still more slowly.

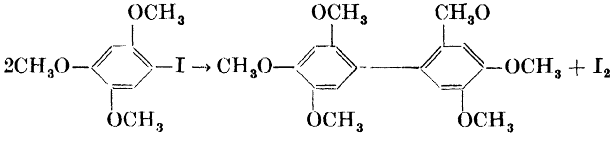
The mechanism of the described migration of halogen may be considered as a direct halogenation by means of halogen-substituted aromatic compounds according to the scheme



$$\begin{matrix} >C^- \\ | \\ X^+ \end{matrix} + \begin{matrix} {}^+H \\ | \\ {}^-C< \end{matrix} \rightleftharpoons \begin{matrix} >C^-\text{—}H^+ \\ \\ X^+\text{—}C^-< \end{matrix}$$

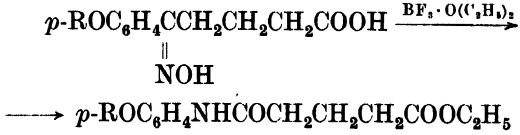
The part played by boron fluoride in this process consists in strengthening the positive reaction of the methoxyl groups on the halogen atoms to the extent of possible exchange between a positively polarized halogen atom of one molecule and a positively polarized hydrogen atom of another. This exchange by different halogens sets in more easily the stronger the halogen is polarized ($I < Br < Cl$).

If in 4-iodoresorcinol dimethyl ether position 6, into which the iodine atom must enter, is occupied by a methyl or methoxyl group, the conversion described above does not take place and other results are obtained. For example if 5-iodotrihydroxybenzene trimethyl ether is left with $BF_3 . O(C_2H_5)_2$ at room temperature it is converted into 2,4,5,2',4',5'-hexamethoxydiphenyl according to the equation



5. REARRANGEMENTS OF COMPOUNDS CONTAINING NITROGEN

Boron fluoride may be used as an isomerizing agent in the Beckmann of oximes and in conversions of diazoamino compounds to aminoazo compounds [63]. Thus, when the oximes of γ-(*p*-methoxy)benzoylbutyric and γ-(*p*-ethoxy) benzoylbutyric acids are boiled with boron fluoride ethyl etherate they easily undergo the Beckmann rearrangement and form the ethyl esters of N-*p*-methoxy- and the corresponding N-*p*-ethoxyphenylglutamic acid according to the reaction

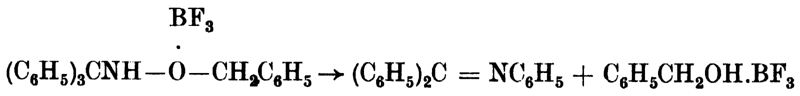


$$p\text{-}ROC_6H_4\underset{\underset{NOH}{\|}}{C}CH_2CH_2CH_2COOH \xrightarrow{BF_3\cdot O(C_2H_5)_2} p\text{-}ROC_6H_4NHCOCH_2CH_2CH_2COOC_2H_5$$

Diphenylketoxime with $BF_3 . O(C_2H_5)_2$ is converted into benzanilide according to the following equation:

$$(C_6H_5)_2C = NOH \xrightarrow{BF_3\cdot O(C_2H_5)_2} C_6H_5NHCOC_6H_5$$

N-triphenylmethyl-O-benzylhydroxylamine, when suspended in ligroin in the presence of boron fluoride, gives benzophenone anil as the main product [65]. It is considered probable that the BF_3 first attacks the hydroxybenzyl group and forms a complex is further rearranged according to the equation



$$(C_6H_5)_3CNH-\overset{\overset{BF_3}{\bullet}}{O}-CH_2C_6H_5 \rightarrow (C_6H_5)_2C = NC_6H_5 + C_6H_5CH_2OH.BF_3$$

6. *Cis-trans*-ISOMERIZATION AND CYCLIZATION

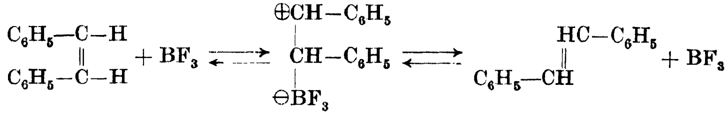
Price and Meister [66] investigated the *cis*- and *trans*- isomerization of stilbene in the presence of BF_3 and found that *cis*-stilbene (0·5 g), dissolved in $BF_3 . O(C_2H_5)_2$ (4 ml) and left for a certain time in the dark at room temperature, is 92 per cent converted into *trans*-stilbene. The conversion depends on the time, which is seen from the following data:

Time (hr)	12	24	30	36	72
Isomerization (%)	10	38·1	74·8	92·3	92·2

The isomerization proceeds considerably more quickly in the solvent CCl_4. For example, if boron fluoride is passed through 0·5 g *cis*-stilbene dissolved in 2 ml CCl_4 for 15 min, a copious residue of *trans*-stilbene separates out; in 18 min the degree of isomerization reaches 93·1 per cent and does not increase any further, which is seen from the following data:

Time (min)	16	18	19
Isomerization (%)	81·0	93·1	93·1

Consequently in both cases the maximum conversion is 92—93 per cent. The mechanism of this isomerization consists in the activation of the carbon atoms of the stilbene which are linked by the double bond, by means of their coordination with the boron fluoride in a coordination compound, as a result of which equilibrium is established between the *cis*- and *trans*-isomers of stilbene:

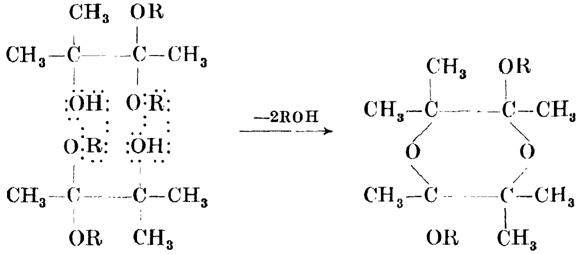


The maximum indicated conversion of *cis*-stilbene to *trans*-stilbene of 92—93 per cent agrees with that found by Kistiakowsky and Smith [67] in the thermal equilibrium between *cis*- and *trans*-stilbene at 340° (*trans*-stilbene content 92—94 per cent) and a little lower than that found by Taylor *et al.* for a temperature of 214° (*trans*-stilbene in equilibrium amounts to 96 per cent) [68].

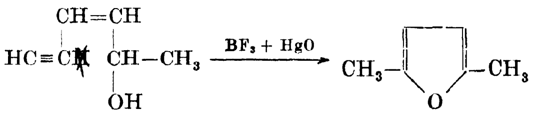
It should be observed that Downing and Wright [69], on repeating the experiments described above on the isomerization of stilbenes, did not obtain any positive results.

Price and Meister's attempts [66] to isomerize diethyl maleate by the action of BF_3 or $BF_3 . O(C_2H_5)_2$ did not lead to any positive results (1 per cent of the ester isomerizes). The absence of the proper effect in the given case is probably explained by the coordination of the boron fluoride molecule with the unshared pair of electrons of the ethereal oxygen atom, and not with the electrons of the carbon atoms connected by the double bond.

In Chapter VIII it was noted that when dimethylethynylcarbinol reacts with alcohols in the presence of BF_3 and HgO, it gives dialkoxyhexamethyldioxanes with 10—15 per cent yield, in addition to the main products, ketals of dimethylacetylcarbinol. As I. N. Nazarov found [70], dialkoxyhexamethyldioxanes are formed by the condensation of two molecules of the corresponding ketals according to the scheme

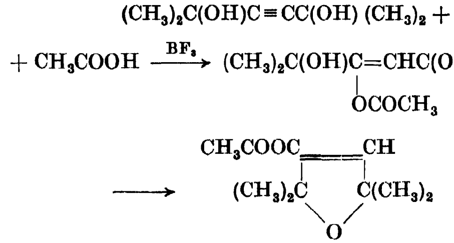


Acetylenic alcohols, for example hexene-3-yne-5-ol-2 [71, 72] with BF_3 + HgO catalyst in methyl alcohol at a temperature of 50—55° is converted into 2,5-dimethylfuran according to the reaction



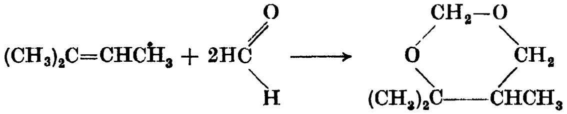
Decene-3-yne-5-ol-2 is cyclized in the same way to 2-methyl-5-*n*-amylfuran [71].

When acetic acid is added to 2,5-dimethylhexyne-3-diol-2,5 in the presence of BF_3 the mono- and diacetates formed undergo cyclization to di- and tetrahydro derivatives of furan [73]. The formation of the monoacetate and its cyclization, according to Yu. S. Zalkind [73], may be represented thus:

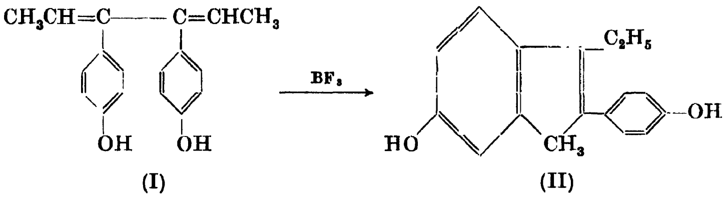


$$(CH_3)_2C(OH)C{\equiv}CC(OH)(CH_3)_2 + + CH_3COOH \xrightarrow{BF_3} (CH_3)_2C(OH)\underset{\displaystyle OCOCH_3}{\underset{|}{C}}{=}CHC(OH)(CH_3)_2$$

Trimethylethylene with formaldehyde and BF_3 in certain conditions forms 1,3-dioxanes [74] according to the reaction



2-Acetoxybutadiene-1,3, formed by the addition of acetic acid to monovinylacetylene in the presence of BF_3, is capable of dimerizing with the same catalyst into 5-acetyl*cyclo*hexene-1-carboxylic acid-2 [75]. 1,4-Dimethyl-2,3-bis-(*p*-hydroxyphenyl)-butadiene-1,3 (I), treated with BF_3 in chloroform for 30 min until a brown oil separates, is converted into 1-methyl-2-(*p*-hydroxyphenyl)-3-ethyl-6-hydroxyindene (II) with a yield of 92 per cent [76]:



(I) (II)

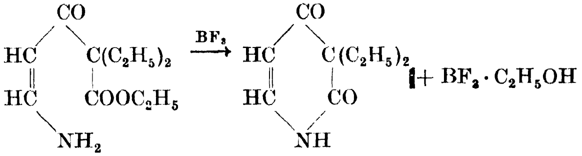
1,4-Dimethyl-2,3-bis-(*p*-acetoxyphenyl)-butadiene-1,3, when treated with boron fluoride as indicated above, gives the diacetate of compound (II); 2,3-bis-(*p*-acetoxyphenyl)-butadiene-1,3 forms 2-(*p*-acetoxyphenyl)-3-methyl-6-acetoxyindene with 80 per cent yield.

Rubber, dissolved in benzene or CCl_4, undergoes cyclization and isomerization on heating with acetic acid for 3 hr to 130—140° in the presence of BF_3 [77]. In addition, depending on the degree of conversion, products are obtained ranging from rubber-like soft ones to a hard, leathery mass which, although it softens at 120°, does not display the softness intrinsic to rubber. The converted rubber adheres tightly to glass, porcelain and metals. From solutions it gives transparent, flexible films which are stable to alkali. It is used instead of oil paints in colouring gypsum and cement, because it is very stable to the influence of cold, heat and moisture. There are indications that for the cyclization of rubber the latex of natural rubber may be treated with boron fluoride [78].

3-Methylpseudoionones are cyclized with boron fluoride with the formation of 6-methyl-α-ionones [79—81]. 2-Methyl-5-(4-methoxynaphthyl)-pentene-2 with boron fluoride forms 1,1-dimethyl-1,2,3,4-tetrahydro-9-methoxyphenanthrene [82]. Naphthalene-1,4-dipropionic acid is converted in the presence of BF_3 into complex cyclization products [83]. Symm.-octahydroanthracene-9-propionic acid gives 11-keto-9,10-*cyclo*pentene-symm.octahydrophenanthrene [84].

Boron fluoride is recommended as a catalyst for the condensation of dienic hydrocarbons (divinyl, *iso*prene) with hydroquinone to chromane derivatives [85].

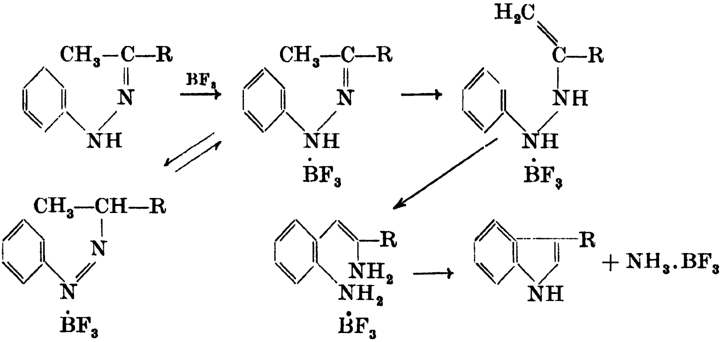
Certain derivatives of aminomethyleneacetoacetic acid or its esters undergo cyclization in the presence of BF_3 and form substituted pyridinediones-2,4. For example, if $H_2NCH = CHCOC(C_2H_5)_2COOC_2H_5$ is heated with BF_3 and concentrated HCl or fuming sulphuric acid the ring is closed and it forms 3,3-diethylpyridinedione-2,4 according to the reaction [86]



Similarly when $HOCH = CHCOC(C_2H_5)_2CONH_2$ is heated with BF_3 it is converted into 3,3-diethylpyridinedione-2,4. 5-Amino-3-keto-4-hexene-1,6-dicarboxylic acid or its esters are cyclized with BF_3 to substituted derivatives of 2,4-pyridinedione carboxylic acid [86].

Phenylhydrazones behave in an interesting way in the presence of boron fluoride. If 36 ml glacial acetic acid and 17·5 g $BF_3 . O(C_2H_5)_2$ are added to 24g freshly distilled *iso*valeraldehyde phenylhydrazone and the mixture is boiled well for 15 min and suitably treated, 3-*iso*propyl indole is obtained with a yield of 13 g, or 60 per cent of the theoretical [87]. In the same way *cyclo*hexanone phenylhydrazone gives 1,2,3,4-tetrahydrocarbazole with a yield of 93 per cent of the theoretical. The cyclization of other phenylhydrazones takes place in a similar way [88, 89]. Ethyl alcohol and benzene may be used as solvents. But the highest yields of products are obtained in acetic acid.

The mechanism of the described reaction [87] consists in the formation of boron fluoride complexes by the phenylhydrazones and their tautomerization with the phenylhydrazo- compounds with subsequent conversion according to the scheme:



Boron fluoride, along with other catalysts, is used for the synthesis of lepidine or 4-methylquinoline from aniline and methylvinylketone with a yield of 28—30 per cent [90, 91]. Acetoacetanilide is converted with BF_3 via difluoroboroacetoacetanilide into 4-methylcarbostyryl-(4-methyl-α-hydroxyquinoline) [92]. Some remarkable conversions of a five-membered ring into a six-membered one in some steroids when they are acylated in the presence of BF_3 are described in Chap. XI.

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CHAPTER X

NITRATION AND SULPHONATION REACTIONS

THE nitration and sulphonation reactions of aromatic compounds in the presence of boron fluoride will in the future probably be of technological interest as well as of laboratory significance. They proceed at temperatures of 40—200°, do not require an excess of nitric and sulphuric acids because BF_3 readily takes up the water evolved in the reaction (aromatic compounds can be nitrated and sulphonated almost quantitatively by the stoichiometric amount of the corresponding acid), they are completed in the course of 0·5—1·5 hr and enable the products to be obtained with a good yield [1]. The boron fluoride may be distilled off from the reaction mass *in vacuo* as the dihydrate $BF_3 . 2H_2O$ and recovered by decomposing the dihydrate. In sulphonation, after driving off the dihydrate, free sulphonic acids remain in the reaction mass in the free state, which is very important because the preparation of free sulphonic acids by the usual method of sulphonation is bound up with great difficulties.

The nitration and sulphonation reactions require for the complete absorption of the water an equimolecular amount of boron fluoride which is seen from the following equations:

$$ArH + HNO_3 + BF_3 \rightarrow ArNO_2 + BF_3 . H_2O$$
$$ArH + H_2SO_4 + BF_3 \rightarrow ArSO_3H + BF_3 . H_2O$$

For recovering the boron fluoride after the reaction another mole of H_2O is added to the mixture and the boron fluoride dihydrate thus formed is distilled off *in vacuo*. If there is no need to recover the boron fluoride, the reaction mixture is diluted with an arbitrary amount of water, neutralized and separated.

All the research workers that have used boron fluoride for nitration and sulphonation regard it as a catalyst in these reactions. The basis for this is the well known experimental data about the ability of boron fluoride to form coordination compounds with nitric and sulphuric acids, by means of which the nitration and sulphonation take place. For example, if boron fluoride is passed into 98 per cent nitric acid, it is absorbed with the evolution of heat, and one molecule of boron fluoride combines with

Table 77. Nitration of aromatic compounds in the presence of BF_3

Nitrated compound	Taken for reaction (moles)			Time of reaction (hr)	Temperature of reaction (°C)	Nitro compound formed
	nitrated substance	HNO_3	BF_3			
Nitrobenzene	0·25	0·30	0·25	1	80—100	*m*-Dinitrobenzene
Benzoic acid	0·25	0·30	0·37	1	80—100	*m*-Nitrobenzoic acid
p-Toluene sulphonic acid	0·10	0·15	0·12	1	100	2-Nitro-4-methylbenzenesulphonic acid
Phthalic anhydride	0·10	0·15	0·12	13	100	3-Nitrophthalic acid

one molecule of nitric acid. The coordination compound

$$\begin{array}{c} H-O-NO_2 \\ \cdot \\ BF_3 \end{array} \quad \text{or} \quad [HOBF_3]^-[NO_2]^+,$$

is evidently formed here. In this the bonds between the oxygen and nitrogen are weakened, which facilitates the separation of the water from the nitric acid and aromatic compound and the entry of the nitro group into the aromatic ring.

Sulphuric acid also absorbs boron fluoride and forms a series of compounds the composition of which depends on the concentration of the acid.

It is known that boron fluoride is a vigorous dehydrating agent, and therefore the possibility is not excluded that in nitration and sulphonation reactions it plays the part of dehydrating agent, forming the hydrate $BF_3 . H_2O$ and the dihydrate $BF_3 . 2H_2O$.

Since nitration and sulphonation reactions have hitherto been carried out in the presence of a large quantity of boron fluoride, sufficient to combine with all the water which separates in the reaction, it is at present impossible to answer the question, what part the boron fluoride plays—whether it is only a dehydrating agent or is at the same time a catalyst. To explain the catalytic role of the boron fluoride it is necessary to study experimentally the course of these reactions in the presence of small amounts of it.

1. NITRATION

The nitration of nitrobenzene, benzoic acid, *p*-toluenesulphonic acid and phthalic anhydride with nitric acid in the presence of BF_3 has been described in the literature [1, 2]. The dinitrobenzene was prepared in the following way: a mixture of 31 g (0·25 mole) nitrobenzene and 19 g (0·3 mole) fuming nitric acid was saturated with 17 g boron fluoride, heating to 80°. It was then decomposed with water, and the dinitrobenzene filtered off and recrystallized from alcohol. The yield of dinitrobenzene was 36·5 g, or 87 per cent of the theoretical. Other examples of nitration are given in Table 77.

A. V. Topchiev [3] used boron fluoride as a catalyst for the nitration of aromatic hydrocarbons with nitrates. A round-bottomed, three-necked flask 1 (Fig. 19), provided with a three-branched adapter 3, the central channel of which served as a passage for the spindle of the stirrer 4, was used as nitration vessel. One of the side branches of the adapter was connected to the condensation-absorption system consisting of a condenser 5 and Tishchenko bottles with ether 6, in which the boron fluoride volatilizing from the reaction mixture was absorbed. The boron fluoride was prepared from CaF_2, B_2O_3 and H_2SO_4 and was then immediately passed through a neck of the flask into the reaction mixture.

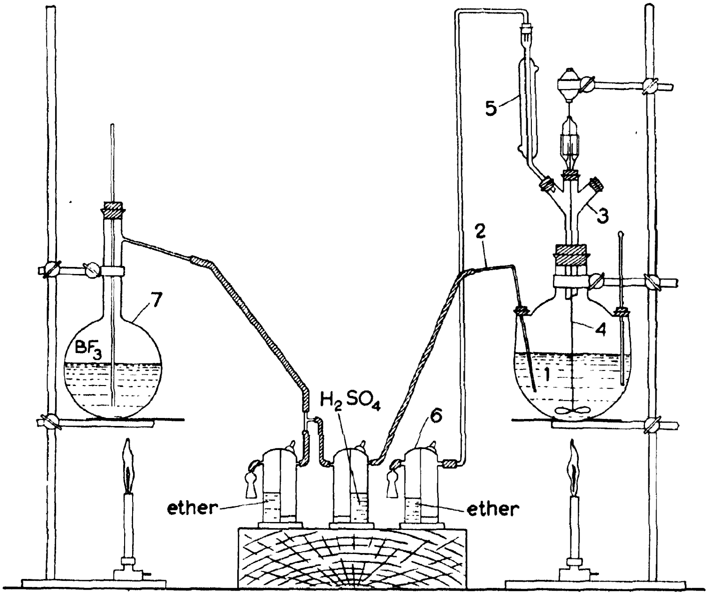


Fig. 19. Apparatus for the nitration of aromatic hydrocarbons with nitrates.

For the nitration, BF_3 obtained from 40 g CaF_2, 20 g B_2O_3 and 200 g H_2SO_4 (sp. gr. 1·84) was generally used for 1 mole hydrocarbon and 50 g anhydrous KNO_3. The results of some experiments are given below.

Nitration of Benzene

Experiments on the nitration of benzene with potassium nitrate in the presence of BF_3 were carried out in the following way: after adding the reagents (0·5 mole KNO_3 and 2 moles benzene), the mixture was stirred and saturated with BF_3 which was passed from a Wurtz flask in which it was prepared. Experiments were carried out both without heating from outside, and with heating (on a water or vaseline bath). In the nitration without heating from outside, the temperature of the reaction mixture

Table 78. *Nitration of benzene with potassium nitrate in the presence of* BF_3 *without heating* [3] *and with different times of experiment* (78 g benzene, 50 g KNO_3 and BF_3)

Time of experiment (min)	Maximum temperature of exothermic reaction (°C)	Yield of nitrobenzene		Recovered benzene		Yield of nitrobenzene per reacted benzene (% of theoretical)	Yield per nitrate (% of theoretical)
		(g)	(% of theoretical per benzene taken)	(g)	(% of benzene taken)		
30	35—36	3	2·4	70	89·6	23·8	4·9
40	35—38	5	4·1	68	87·2	31·7	8·1
50	35—38	8	6·5	63	80·6	33·8	13·0
120	45—58	12	9·7	58	74·3	38·1	19·5
150	55—57	17	13·8	57	73·0	51·4	27·6
180	55—57	21	17·0	54	69·2	55·5	34·1
300	55—57	20·6	16·7	53	67·9	52·3	33·5

Table 79. *Nitration of benzene with potassium nitrate in the presence of* BF_3 *at different temperatures* [3] *and the time of the experiment being* 3 hr (78 g benzene, 50 g KNO_3 and BF_3)

Temperature (°C)	Yield of nitrobenzene		Recovered benzene		Yield of nitrobenzene per reacted benzene (% of theoretical)	Yield per nitrate (% of theoretical)
	(g)	(% of theoretical per benzene taken)	(g)	(% of benzene taken)		
Without heating	21·0	17·1	55	70·5	57·9	34·1
Maximum temperature of exothermic reaction 57°	21·2	17·2	54	69·2	56·0	34·4
90—95° (temperature of bath)	11·0	9·0	63	80·8	46·5	17·9
90—95° (temperature of bath)	12·2	9·9	62	79·5	48·3	19·8

was rapidly increased to 34—38° and then, more slowly, to 55—57°, on account of the exothermic nature of the process.

When the saturation with boron fluoride was complete, the reaction mixture was of a dark brown colour, and separated into a liquid part and a solid residue (at the bottom of the flask). The liquid part was separated from the residue, washed with water and then with soda solution, and after drying over calcium chloride it was subjected to distillation (at first benzene distilled, and then at 207—210° nitrobenzene). The solid residue was then distilled in steam to recover the nitrobenzene adsorbed by it.

Results of experiments on the nitration of benzene with potassium nitrate in the presence of BF_3 are given in Tables 78 and 79.

Nitration of Toluene and m-*Xylene*

Results of experiments on the nitration of toluene and *m*-xylene with potassium nitrate in the presence of BF_3 are given in Tables 80 and 81.

Table 80. *Nitration of toluene with* KNO_3 *in the presence of* BF_3 [3] (92·1 g toluene, 50 g KNO_3 and BF_3)

Maximum temperature of exothermic reaction (°C)	Yield of nitrotoluene		Recovered toluene		Yield of nitrotoluene per reacted toluene (% of theoretical)	Yield per nitrate (% of theoretical)
	(g)	(% of theoretical per toluene taken)	(g)	(% of toluene taken)		
40	23·8	17·4	71	77·1	76·2	34·7
40	24·3	17·7	69	75·0	70·9	35·5

Table 81. *Nitration of* m-*xylene with* KNO_3 *in the presence of* BF_3 [3] (11 g *m*-xylene, 10 g KNO_3 and BF_3)

Maximum temperature of exothermic reaction (°C)	Yield of mononitroxylene		Yield of dinitroxylene	
	(g)	(% of theoretical per nitrate taken)	(g)	(% of theoretical per nitrate taken)
35	3·6	23·8	1·1	5·6
35	3·4	22·6	1·3	6·6

The results of the experiments show that benzene, toluene and *m*-xylene are nitrated by potassium nitrate in the presence of boron fluoride in a similar way to the nitration by nitrates in the presence of $AlCl_3$. The best conditions (with a yield of nitro-product of about 35 per cent of the nitrate) are attained by carrying out the reaction for 3 hr without heating. Increase of temperature lowers the yield of nitro-product, which is explained by the decomposition of the complex formed by the boron fluoride with the aromatic compound at high temperature.

Preparation of Dinitro Derivatives

To examine the possibility of the introduction of several nitro groups into the aromatic ring by the action of nitrates in the presence of BF_3 A. V. Topchiev [3] studied the nitration of nitrobenzene with potassium nitrate and found that if the reaction is carried out without heating, a low yield of dinitrobenzene (1·2 per cent calculated on the nitrate and 18 per cent on the nitrobenzene) is obtained. If the reaction mixture is heated to 95—100° the yield of dinitrobenzene is increased to 9 per cent calculated on the nitrate and to 40 per cent on the nitrobenzene which has entered into the reaction.

Thus, in nitration with KNO_3 in the presence of BF_3 the introduction of the second nitro group into the aromatic ring takes place with considerably more difficulty than the introduction of the first.

The mechanism of the nitration of aromatic compounds with nitrates in the presence of boron fluoride, in A. V. Topchiev's opinion, includes the following four stages:

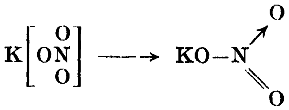
(1) conversion of the true form of the nitrate into the pseudoform;

(2) formation of a complex of the nitrated substance with the catalyst;

(3) formation of a ternary complex, aromatic compound—catalyst—nitrate;

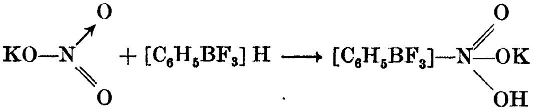
(4) decomposition of the ternary complex, leading to the formation of an aromatic nitroderivative and recovery of the catalyst (in addition the hydroxide of the metal, the nitrate of which is the nitrating agent, separates as one of the reaction products).

The nitration of benzene with KNO_3 in the presence of BF_3 may be represented by the following scheme:

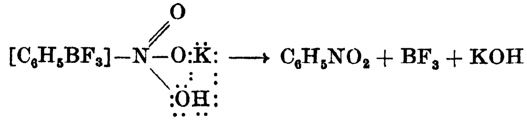


$$\mathrm{K}\begin{bmatrix} & \mathrm{O}\\ \mathrm{O} & \mathrm{N}\\ & \mathrm{O}\end{bmatrix} \longrightarrow \mathrm{KO{-}N}\begin{matrix}\nearrow \mathrm{O}\\ \searrow\!\!\searrow \mathrm{O}\end{matrix} \qquad (1)$$

$$C_6H_6 + BF_3 \longrightarrow [C_6H_5BF_3]H \qquad (2)$$



$$\mathrm{KO{-}N}\begin{matrix}\nearrow \mathrm{O}\\ \searrow\!\!\searrow \mathrm{O}\end{matrix} + [C_6H_5BF_3]H \longrightarrow [C_6H_5BF_3]{-}\mathrm{N}\begin{matrix}/\!\!/\ \mathrm{O}\\ {-}\mathrm{OK}\\ \diagdown\ \mathrm{OH}\end{matrix} \qquad (3)$$



$$[C_6H_5BF_3]{-}\mathrm{N}\begin{matrix}/\!\!/\ \mathrm{O}\\ {-}\mathrm{O{:}\ddot{K}{:}}\\ \diagdown\ \mathrm{{:}\ddot{O}H{:}}\end{matrix} \longrightarrow C_6H_5NO_2 + BF_3 + KOH \qquad (4)$$

2. SULPHONATION

Benzene was sulphonated in the following way: boron fluoride was passed into a mixture of 78 g (1 mole) benzene and 104 g (1 mole) 94 per cent sulphuric acid for 1·5 hr with vigorous stirring. After the absorption of 66 g BF_3 the reaction mass was heated under reflux condenser on the water bath. The reaction product, a transparent homogeneous mixture of slightly yellowish tint, contained in all 1·1 g of benzene which had not entered into the reaction. The sulphonation process was 98 per cent complete by the time that 42 per cent of the benzene had reacted in the control experiment with sulphuric acid alone (without catalyst) [1].

On neutralizing the aqueous solution of sulphonic acid with lime, its calcium salt separated out, which, as the results of the analysis show, consisted of calcium benzene sulphonate with a small admixture of disulphonate.

In a similar way, toluene is sulphonated with the formation of *p*-toluene sulphonic acid.

In the sulphonation of naphthalene boron fluoride was passed into a vigorously stirred mixture, consisting of 1·52 moles 94 per cent sulphuric acid and 1·50 moles naphthalene at a temperature below 30° for 8 hr until 108 g BF_3 were absorbed. The product was diluted with water, neutralized with soda, after which 263 g sodium naphthalene α-sulphonate crystallized out. The amide of this sulphonic acid has m. p. 145—147°, which corresponds to the α-isomer.

If the sulphonation reaction is carried out at 160—165°, the β-isomer is mainly obtained, together with a small amount of $\beta\beta$-dinaphthylsulphone.

Phenol was sulphonated by passing BF_3 into a mixture of 94 g (1 mole) phenol and 98 g 100 per cent sulphuric acid for 1·5 hr until 28 g BF_3 had been adsorbed. The introduction of boron fluoride caused an instantaneous rise of temperature to 80°, and the temperature was further raised to 100° by heating the reaction flask on a water bath. Then the reaction mixture was diluted with water to 1 l., neutralized with soda, brought to the boil, saturated with cooking salt and filtered. When the solution was allowed to stand, about 170 g sodium phenolsulphonate gradually crystallized.

The sulphonation of β-naphthol, α- and β-naphthylamines, was studied [4]. On heating a mixture of α-naphthylamine (36 g), concentrated sulphuric acid (144 g) and boron fluoride (26 g) to 75-80° for 1 hr, naphthionic acid is obtained with a yield of 86 per cent. β-Naphthylamine, heated to 50—55° for 30 min with sulphuric acid in the presence of boron fluoride, forms a mixture of sulphonic acids consisting of 48 per cent 2-aminonaphthalene-8-sulphonic acid and 52 per cent 2-aminonaphthalene-5-

sulphonic acid. The sulphonation of β-naphthylamine at a temperature of 20° gives a mixture of sulphonic acids consisting of 56 per cent 2-aminonaphthalene-8-sulphonic acid and 44 per cent 2-aminonaphthalene-4-sulphonic acid. The sulphonation of β-naphthylamine at a temperature of 80° leads to the formation of 2-aminonaphthalene-8-sulphonic acid and 2-aminonaphthalene-5-sulphonic acid in amounts corresponding to 33 and 67 per cent.

When β-naphthol is sulphonated with sulphuric acid in the presence of boron fluoride at a temperature of 80—90° for 2 hr, 2-hydroxynaphthalene-3,6-disulphonic acid is obtained as the main product.

Thus, the amino group directs sulphonic groups to the α-position and the hydroxyl group directs them to the β-position of the naphthalene ring.

By the method described it is also possible to sulphonate heterocyclic compounds with a mixture of H_2SO_4 and BF_3 [5]. Carbazole (42·5 g), treated with 94 per cent sulphuric acid (54 g) and BF_3 (29 g) at a temperature of 100°, gives mainly carbazole disulphonic acid.

Boron fluoride is not very effective in the sulphonation of chlorobenzene, nitrobenzene and benzoic acid.

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CHAPTER XI

CONDENSATION REACTIONS IN THE PRESENCE OF BORON FLUORIDE

1. CONDENSATION OF CARBON MONOXIDE WITH OLEFINES, ALCOHOLS AND ETHERS

THE synthesis of hydrocarbons from carbon monoxide and hydrogen is well known. In the U.S.S.R. it has been successfully carried out by a number of scientists. Interesting investigations in this field have been collected by Ya. T. Eidus in a series of reviews published in the journal *Uspekhi Khimii* [1].

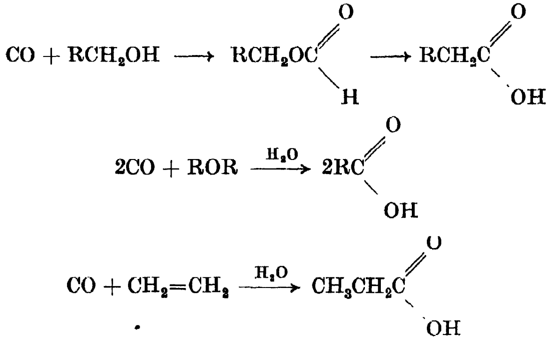
During the last 10—15 years many patents have been published recommending the use of BF_3 as a catalyst in the condensation of carbon monoxide with olefines, alcohols and ethers, as a result of which, depending on the conditions, organic acids or esters are obtained [2—12]. The condensation may be carried out in the liquid or the vapour phases, at atmospheric or increased pressure and different temperatures, and boron fluoride may be used [8—18] either in the form of coordination compounds with mineral acids [2, 3] or with water [5, 7, 19—30].

This method is very suitable for the synthesis of the lower aliphatic acids, acetic and propionic. Thus, when carbon dioxide is condensed with methyl alcohol in the presence of $BF_3 . 2H_2O$ at a temperature of 260° and pressure of 700 atm acetic acid is obtained with 75 per cent yield [21]. When a mixture of carbon monoxide, boron fluoride ethyl etherate and $BF_3 . H_2O$ is heated at a temperature of 170° and increased pressure, propionic acid is obtained [22]. Acids are obtained in good yield on heating carbon monoxide and boron fluoride coordination compounds to 180—250° with alcohols or compounds capable of giving alcohols on hydrolysis [16]. In many patents it is pointed out that the condensation proceeds particularly effectively if the boron fluoride is used as hydrates in which there is from 1 to 5 moles water per mole BF_3.

Polyhydric alcohols—ethylene glycol, propylene glycol, glycerol and others, on treatment with carbon monoxide in the presence of boron fluoride are converted into polybasic acids [15]. Unsaturated and hydroxymonocarboxylic acids with carbon monoxide in the presence of boron fluoride hydrates at a temperature of 75—300° and pressure of 400—1000 atm give dibasic carboxylic acids [31, 32].

Esters of β-alkoxypropionic acid and carbon monoxide form esters of succinic acid [33]. Esters of the general formula $ROCH_2OCH_2COOR$, when treated with carbon monoxide in the presence of boron fluoride give esters of diglycollic acid of the formula $O(CH_2COOR)_2$ [34]. Similarly olefines, for example ethylene or propylene, on heating with carbon monoxide under pressure in the presence of BF_3 and water are converted into the corresponding acids [35].

All these reactions must no doubt occupy an important place in the numerous synthetic methods for preparing organic acids and their esters owing to the comparative simplicity and the possibility of recovering the catalyst from the reaction mixture. In general they may be represented by the equations:



$$\mathrm{CO + RCH_2OH \longrightarrow RCH_2OC(=O)H \longrightarrow RCH_2C(=O)OH}$$

$$\mathrm{2CO + ROR \xrightarrow{H_2O} 2RC(=O)OH}$$

$$\mathrm{CO + CH_2{=}CH_2 \xrightarrow{H_2O} CH_3CH_2C(=O)OH}$$

sec.-and *tert.*-Mono- and dihaloalkyls with carbon monoxide in the presence of BF_3 at a temperature from −28 to 25° and a pressure of 10−700 atm are converted into the corresponding haloanhydrides. Thus, *tert.*-butyl chloride and carbon monoxide in the presence of BF_3 at 0° and a pressure of 700 atm form the chloroanhydride of trimethylacetic acid with 49 per cent yield [36]. 1,2-Dichloropropane and carbon monoxide at a temperature from −28 to 18° and a pressure of 600 atm in the presence of HF and BF_3 form the fluoroanhydride β-chloroisobutyric acid with 88 per cent yield [37] according to the reaction

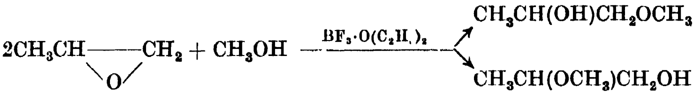
$$\mathrm{CH_3CHClCH_2Cl + CO + HF \xrightarrow{BF_3} ClCH_2CH(CH_3)COF}$$

Aromatic hydrocarbons and carbon monoxide in the presence of $BF_3 + HF$ catalyst at a temperature from −80 to 50° and increased pressure are converted into the corresponding aromatic aldehydes [38, 39]

2. REACTIONS OF α-OXIDES

The Reaction of α-Oxides with Alcohols

This reaction was studied in detail by A. A. Petrov [40, 41]. The author studied the reaction of the oxides of ethylene, propylene, pseudobutylene, *iso*butylene, *cyclo*hexene, epichlorhydrin and the methyl ether of glycidol with methyl and ethyl alcohols in the presence of catalysts of boron fluoride ethyl etherate and alcoholates. By comparing the constants of the products obtained with those described in the literature it was found that in the presence of basic catalysts (alcoholates) alcohols are added on to the unsymmetrical α-oxides according to the Markownikoff rule with the formation of ethers of primary alcohols, but in the presence of $BF_3 . O(C_2H_5)_2$ the addition goes to a considerable extent against the Markownikoff rule, and therefore a mixture of ethers of primary and secondary alcohols is obtained. Later [42] these data were confirmed. For propylene oxide and methyl alcohol the reaction may be represented by the following equation:



$$2CH_3\underset{\diagdown O \diagup}{CH\text{———}CH_2} + CH_3OH \xrightarrow{BF_3\cdot O(C_2H_5)_2} \begin{cases} CH_3CH(OH)CH_2OCH_3 \\ CH_3CH(OCH_3)CH_2OH \end{cases}$$

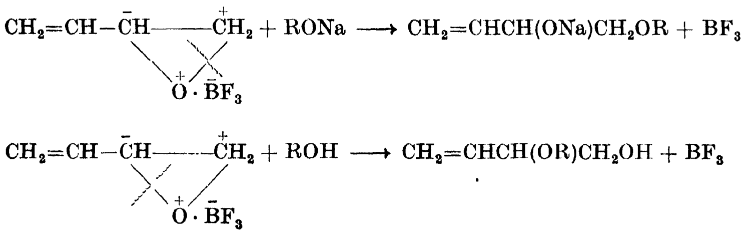
The $BF_3 . O(C_2H_5)_2$ catalyst in this reaction has a fairly high efficiency even when it is used in the amount of 0·015 per cent of the weight of the reagents. Of the oxides, ethylene oxide and epichlorhydrin react the most slowly with alcohols [40]. When a fivefold excess of alcohol is used the reaction products are monoethers of diols. With a smaller excess of alcohol polyethers of glycols, carbitols, are also formed. With a larger excess of alcohols the yield of glycol monomethyl ethers amounted 75—80 per cent of the oxide, but the yield of ethylene glycol monoethyl ether was equal to 68·5 per cent.

Similar conclusions were arrived at by Chimwood and Freure [43], who found that when propylene oxide is reacted with ethyl alcohol in 1 : 5 ratio in the presence of 0·1 per cent BF_3 for 2 hr at a temperature of 50—60°, 1-ethoxy-2-propanol is formed with a yield of 45·1 per cent and 2-ethoxy-1-propanol with a yield of 29·0 per cent. Besides these products, dipropylene glycol ethyl ether is obtained with a yield of 20·4 per cent. There are also patent data about the use of boron fluoride catalyst for this reaction [44].

F. G. Ponomarev [45, 46], by reacting epichlorhydrin with a five-to eightfold excess of methyl, ethyl, *iso*propyl and *n*-butyl alcohols in the presence of 0·05—0·5 per cent of the catalyst $BF_3 . O(C_2H_5)_2$, obtained the ethers of the specified alcohols with α-monochloroglycerol with a yield of 77, 71, 67 and 77 per cent respectively. The author also assumes that the reaction proceeds only in one direction with the formation of ethers of the general formula $ClCH_2CH(OH)CH_2OR$ and the possible second direction of the reaction with the formation of ethers of the formula $CH_2ClCH(OR)CH_2OH$ is not recorded.

According to the results of M. G. Vladimirov and A. A. Petrov [47] glycidol methyl and ethyl ethers add alcohols both in the presence of basic catalysts (alcoholates) and in the presence of boron fluoride ethyl etherate with the formation of the same glycerol α, γ-diethers, but the ethers obtained in the presence of $BF_3 . O(C_2H_5)_2$ contain about 15 per cent of glycerol α, β-diethers.

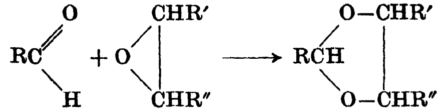
Divinyl oxide in the presence of alcoholates, like propylene oxide, adds alcohols in accordance with the Markownikoff rule with the formation of primary ethers of erythritol, but in the presence of $BF_3 . O(C_2H_5)_2$ the addition of alcohols to divinyl oxide proceeds contrary to the Markownikoff rule with the formation of secondary ethers of erythritol [48]. To explain the order of addition of alcohols to divinyl oxide, A. A. Petrov put forward a hypothesis according to which alkaline catalysts, particularly alcoholates, simply increase the reactivity of the alcohols; their catalytic action is not connected with the deformation of the bond and depends only on the easy addition according to the Markownikoff rule as compared with free alcohols, but BF_3 acts in such a way that complex compounds are formed with the oxides. As a result of this coordination the link between oxygen and carbon is weakened, and the oxide takes the form of an oxonium compound with a positively charged trivalent oxygen and reacts with alcohols with the formation of ethers of secondary alcohols. This addition may be expressed by the following equations:

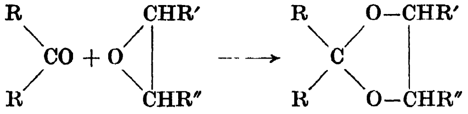

CH₂=CH–CH——CH₂ + RONa ⟶ CH₂=CHCH(ONa)CH₂OR + BF₃
O · BF₃
CH₂=CH–CH——CH₂ + ROH ⟶ CH₂=CHCH(OR)CH₂OH + BF₃
O · BF₃

Similarly unsaturated alcohols react with α-oxides. Allyl alcohol with ethylene oxide in the presence of $BF_3 . O(C_2H_5)_2$ forms allyloxyethanol $CH{=}CHCH_2OCH_2CH_2OH$ [49]. Polyhydric alcohols are capable of entering into reaction with α-oxides in the presence of $BF_3 . O(C_2H_5)_2$ [50, 51].

The Reaction of α-Oxides with Aldehydes and Ketones

According to the results of A. A. Petrov [40], the catalysts anhydrous aluminium chloride, ferric chloride and antimony trichloride are not suitable for the condensation of α-oxides with carbonyl compounds. The reaction of α-oxides with aldehydes and ketones in the presence of boron fluoride ethyl etherate leads to the formation of cyclic acetals, dioxolanes, according to the reaction





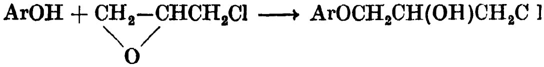
In the given case, however, the reaction is accompanied by strong polymerization of the oxides, and therefore the condensation products, dioxolanes, are obtained in comparatively small yield. For example, the oxides of ethylene, propylene, pseudobutylene and epichlorhydrin with acetone give dioxolanes with a yield of 12, 22, 35 and 58 per cent respectively [52]. In the reaction with diethyl- and ethylpropyl ketones the yield of the corresponding dioxolanes does not exceed 2—3 per cent. Butyraldehyde with pseudobutylene oxide forms 2-propyldioxolane with a yield of 24 per cent of the theoretical [40].

The Reaction of a-Oxides with Carboxylic Acids and their Esters

Monobasic carboxylic acids containing four or more carbon atoms in the molecule, like alcohols, aldehydes and ketones, condense with α-oxides in the presence of BF_3 with the formation of esters. Thus, butyric, valeric, oleic and palmitic acids with epichlorhydrin form the corresponding esters of glycerol monochlorhydrin [53, 54]. Hydroxyacids or their esters, for example dibutyl malonate and triethyl citrate, with propylene oxide in the presence of BF_3 form the corresponding condensation products, which are used as synthetic lubricating oils [55].

Reaction of a-Oxides with Phenols and their Ethers

When phenol [56], cresols, thymol, *o-cyclo*hexylphenol and *p*-bromophenol [57, 58] are reacted with epichlorhydrin in the presence of BF_3 at a temperature not above 0°, they form as main product epichlorhydrin monoaryl ethers with a yield of 42—68 per cent according to the reaction



$$ArOH + \underset{\diagdown O \diagup}{CH_2{-}CH}CH_2Cl \longrightarrow ArOCH_2CH(OH)CH_2Cl$$

The study of the influence of the concentration of epichlorhydrin, the catalysts BF_3 and $BF_3 . 2H_2O$ and also the nature of the solvent on this reaction showed that the yields of glycerol α-monochlorhydrin γ-aryl ethers increase with increase of the relative quantities of phenols. An increase in the quantity of BF_3 catalyst to a known limit also increases the yield of the ether of glycerol monochlorhydrin. A high percentage of BF_3 sharply lowers the yield of these products, as is clearly seen from the data of Table 82 on the condensation of 0·25 mole epichlorhydrin and 1 mole phenol at a temperature of 0° [58].

Table 82. *Influence of the amount of* BF_3 *catalyst on the yield of glycerol monochlorohydrin phenyl ether* [58]

BF_3 (g)	Yield of $C_6H_5OCH_2CH(OH)CH_2Cl$ calculated on epichlorhydrin (g)	(%)	Yield of higher products (%)
1·0	25·05	53·9	15·0
2·0	26·00	56·5	13·0
3·2	25·30	54·3	14·0
9·5	12·50	26·2	20·5

The use of boron fluoride dihydrate instead of BF_3 lowers the yield of basic product. As is evident, in this reaction even more complex compounds are obtained which are apparently formed from one molecule of phenol and two or more molecules of epichlorhydrin. Guaiacol in similar conditions gives only higher products. *o*-Nitrophenol does not enter into a condensation reaction with epichlorhydrin [57].

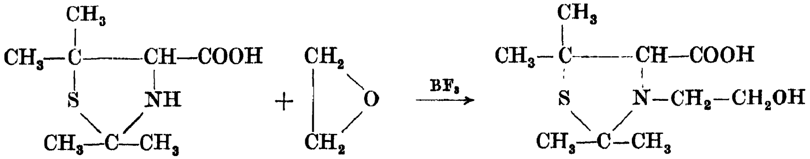
*cyclo*Hexene oxide and phenol, when treated with boron fluoride for 10 hr at a temperature of 40—70°, form *p*-*cyclo*hexylphenol (a small amount) and *cyclo*hexane diol-1,2 (*trans*-isomer) [59].

Alkyl ethers of phenols condense with *a*-oxides, but they form more complex mixtures of reaction products and with lower yield. *cyclo*Hexene oxide with anisole in the presence of BF_3 at a temperature of 50° gives *p*-*cyclo*hexylanisole with 8 per cent yield, and also 1,3-dianisyl*cyclo*hexane and 4,4′-dimethoxy-*m*-terpenyl [59].

Reaction of a-Oxides with Compounds containing Nitrogen or Sulphur

If ethylene oxide and a boron fluoride coordination compound with trimethylamine are heated to 40—70° for 4 hr, they form a product $(CH_3)_3\overset{+}{N}CH_2CH_2\overset{-}{O}\,.\,BF_3$ (m. p. 296—298°) with 100 per cent yield [60]. The boron fluoride coordination compound with pyridine $C_5H_5N\,.\,BF_3$ and ethylene oxide in pyridine at a temperature of 0° give 100 per cent yield of the addition product $C_5H_5\overset{+}{N}CH_2CH_2OBF_3$ (m. p. 131—132°), but with epichlorhydrin they form a 63 per cent yield of the compound $C_5H_5\overset{+}{N}CH_2CH(O\overset{-}{B}F_3)CH_2Cl$ with m. p. 164—165° (recrystallized from liquid sulphur dioxide) [60].

Ethylene oxide and 2,2,5,5-tetramethyl-4-carboxythiazolidine are converted in the presence of BF_3 into 3-(2-hydroxyethyl)-2,2,5,5-tetramethyl-4-carboxythiazolidine according to the reaction [61]



3. VARIOUS REACTIONS FOR PREPARING ETHERS AND ESTERS

Dehydration of Alcohols to Ethers

As noted in Chap. II, when monohydric alcohols saturated with boron fluoride are heated, ethers are obtained as boron fluoride coordination compounds [62, 63]. This reaction proceeds most smoothly for the lower alcohols. However, even in the case of methyl alcohol, it is accompanied by a number of side reactions. In spite of this the boron fluoride method of synthesis of methyl ether is the most convenient [62, 64], because it allows the ether to be obtained as a coordination compound with BF_3, a liquid with b. p. 128°. In all other methods, free methyl ether is formed in gaseous form (b. p. —25°), which often makes it difficult to use. The boron fluoride synthesis is carried out in the following way: absolute methyl alcohol is saturated with boron fluoride until a coordination compound of the composition $BF_3 . CH_3OH$ is formed, which is then boiled under reflux condenser for 3 hr and the mixture is subjected to rectification. About 87° methoxyboron fluoride CH_3OBF_2 distils, and at 128° boron fluoride methyl etherate. The yield of this is more than 50 per cent. Higher alcohols in the presence of BF_3 are usually dehydrated with the formation of olefines, which polymerize to oily products.

Esterification of Alcohols with Carboxylic Acids

The property of boron fluoride to react vigorously with alcohols and carboxylic acids and form with them complex compounds with appreciably increased acidity makes it a particularly good catalyst for the esterification of alcohols with carboxylic acids. If acetic acid and ethyl alcohol are heated under a reflux condenser in the presence of 1—2 per cent of the coordination compound $BF_3 . 2CH_3COOH$ they form ethyl acetate with a yield of 47—50 per cent of the theoretical [65, 66]. It is interesting that if the quantity of catalyst here is increased to more than 1—2 per cent, and the time of heating is also increased from 1 to 10 hr the yield of ethyl acetate does not increase. If 7 g BF_3 is passed into a mixture of 59·4 g propyl alcohol and 60 g glacial acetic acid and the mixture is then heated under a reflux condenser for half an hour, propyl acetate is obtained with a yield of 53·5 per cent. Propionates of the corresponding alcohols are obtained with a yield from 33 to 66 per cent from propionic acid and ethyl, propyl, *n*-butyl and *n*-amyl alcohols in the presence of BF_3 coordination compounds with propionic acid [65].

The yields of esters for the different acids in this reaction increase in the same order as in the addition of acids to olefines, and do not differ from them greatly. Thus, if *iso*propyl alcohol is boiled for 3 hr with the corresponding acids in the presence of BF_3, or if propylene is passed into a mixture of 3 g BF_3 and 1 mole acid [67] for 16 hr at a temperature of 70°, *iso*propyl ether is formed with the following yields:

Acid	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH	C_6H_5COOH
Yield of ester from alcohol and acid (%)	16·8	38·8	48·6	57·8	60·0
Yield of ester from propylene and acid (%)	7·0	34·2	39·5	48·7	88·0

Methyl alcohol is esterified more easily with carboxylic acids than ethyl and *iso*propyl alcohols, and forms esters of the corresponding acids with higher yields. If 1·5 moles methyl alcohol and 0·75 mole carboxylic acid are heated for 45 min at 64° in the presence of 7 g boron fluoride ethyl etherate, then methyl acetate, chloroacetate, dichloroacetate, trichloroacetate, propionate, benzoate and phenylacetate are obtained with yields of 56, 65, 70, 73, 44, 37 and 86 per cent respectively [68].

Polyhydric alcohols and aliphatic acids containing not less than twelve carbon atoms in the molecule may be condensed in the presence of boron fluoride [69].

Substituted aromatic acids are appreciably more difficult to esterify with alcohols in the presence of BF_3. Salicylic acid with alcohols in the presence of BF_3, as with olefines, first forms esters which on prolonged reaction isomerise to alkyl substituted derivatives of salicylic acid which are capable of entering into reaction with a second molecule of alcohol and finally giving alkyl-substituted salicylates [70]. The yield of esters of aromatic substituted acids depends on the nature of the substituent in the ring and the amount of BF_3 catalyst. If the quantity of BF_3 is increased the yield of esters usually increases to a certain maximum, after which a further increase in the amount of catalyst not only does not increase the yield of ester but is sometimes harmful because it favours the intensification of side reactions [71]. However, the limiting quantity of BF_3 is not the same for different acids and depends on the nature of the substituents in the ring. To attain the maximum yield of ester, some substituted benzoic acids require four to five times more boron fluoride than the acid itself. For example, to prepare methyl benzoate with the maximum yield of 85 per cent it is necessary to introduce 14 g BF_3 into the reaction per 0·5 mole benzoic acid, but in order to prepare methyl *p*-aminobenzoate with 53 per cent yield, it is necessary to use 3 moles BF_3 per 1 mole acid. Methyl anthranilate is obtained with a yield of 85 per cent on introducing 2 moles BF_3 per 1 mole acid into the reaction [71]. To prepare esters of *p*-aminosalicylic acid with good yields, 4·5 moles $BF_3 . O(C_2H_5)_2$ are used per 1 mole acid [72]. This excess of boron fluoride required in the esterification of aromatic amino- acids with alcohols is explained by its great affinity for the amino group and by the formation of stable coordination compounds with acids in which the BF_3 loses its catalytic activity.

The influence of the nature of the substituent in the benzene ring and other factors on the yield of aromatic esters is well illustrated by the data of Table 83.

The esterification of 2-(9′-carboxynonyl)-3-hydroxy-1,4-naphthoquinone with methyl alcohol in the presence of $BF_3 . O(C_2H_5)_2$ is described in the literature [73].

Cleavage of Ethers

In textbooks on organic chemistry ethers are usually described as compounds which are very stable and enter into reaction with difficulty. However, in the presence of boron fluoride and other metal halides they can be split up by acid haloanhydrides, anhydrides and carboxylic acids to form esters.

The cleavage of ethers by acid haloanhydrides in the presence of BF_3, $SnCl_4$, $SbCl_5$ and $SnBr_4$ was studied in detail by L. M. Smorgonskii [74]. It was found by the author that boron fluoride is a highly effective catalyst only in the cleavage of alkyl ethers with acid fluoroanhydrides, and feebly effective in the reaction of alkyl ethers with acid chloro- and bromoanhydrides. Thus, for example, ethyl ether in the form of a BF_3 coordination compound is decomposed by benzoyl fluoride with the formation of ethyl benzoate with a yield of 80 per cent, by benzoyl bromide in similar conditions with the formation of the same ethyl benzoate with a yield of 20 per cent, and by benzoyl chloride with a yield of 39 per cent according to the reaction.

$$RCOX + R'OR' \rightarrow RCOOR' + R'X \qquad (X = F,\ Cl,\ Br)$$

Smorgonskii explains the reduced efficiency of BF_3 as a catalyst in the case of acid chloro- and bromoanhydrides by the steric hindrance of the coordination of the halogen atom of the haloanhydride to the central boron atom of the catalyst.

Table 83. *Esterification of aromatic acids with alcohols in the presence of* BF_3

Reagent				BF_3 (g)	Time of reaction (hr)	Ester	Yield of ester (%)
Acid	(moles)	Alcohol	(moles)				
Benzoic	0·5	Methyl	1·0	14·0	0·5	Methyl benzoate	85·3
Benzoic	0·5	*iso*Propyl	1·0	9·6	0·83	*iso*Propyl benzoate	60·0
Benzoic	0·5	*n*-Butyl	1·2	18·6	0·83	Butyl benzoate	86·8
Benzoic	0·5	*iso*Butyl	1·0	13·0	0·83	*iso*Butyl benzoate	81·8
Benzoic	0·5	*sec.*-Butyl	1·0	14·0	0·83	*sec.*-Butyl benzoate	26·5
Benzoic	0·5	*tert.*-Butyl	1·0	14·0	0·83	*tert.*-Butyl benzoate	0·0
p-Nitrobenzoic	0·125	Methyl	2·19	17·5*	3·00	Methyl *p*-nitrobenzoate	100
p-Nitrobenzoic	0·125	Methyl	2·19	3·4*	5·00	Methyl *p*-nitrobenzoate	93·2
p-Nitrobenzoic	0·50	Methyl	2·19	3·4*	6·00	Methyl *p*-nitrobenzoate	88·3
p-Aminobenzoic	0·25	Methyl	4·38	56·6*	3·00	Methyl *p*-aminobenzoate	53·0
p-Aminobenzoic	0·25	Methyl	4·38	68·0*	3·00	Methyl *p*-aminobenzoate	40·3
o-Aminobenzoic	0·50	Methyl	1·60	68·0	4·50	Methyl *o*-aminobenzoate	85·4
o-Chlorobenzoic	0·125	Methyl	2·19	9·5*	3·00	Methyl *o*-chlorobenzoate	70·6
o-Hydroxybenzoic	0·50	Methyl	2·10	66·0	1·25	Methyl *o*-hydroxybenzoate	55·0
o-Hydroxybenzoic	0·5	*iso*Butyl	1·00	17·0	2·00	*iso*Butyl *o*-hydroxybenzoate	74·2
p-Aminosalicylic	1·0	Methyl	1 l.	565* ml	10 days	Methyl *p*-aminosalicylate	74·0
p-Aminosalicylic	1·0	Ethyl	1 l.	565* ml	10 days	Ethyl *p*-aminosalicylate	71·0
p-Aminosalicylic	1·0	*iso*Propyl	1 l.	565* ml	30 days	*iso*Propyl *p*-aminosalicylate	75·0

* The catalyst was used as boron fluoride ethyl etherate

Similar behaviour of BF_3 as a catalyst was noted also in the alkylation of aromatic hydrocarbons with alkyl halides. Thus, toluene is cycloalkylated by *cyclo*hexyl fluoride in the presence of BF_3, but does not react with *cyclo*hexyl chloride in similar conditiones [75].

More effective catalysts for the cleavage of alkyl ethers by acid chloroanhydrides are $ZnCl_2$, $AlCl_3$, $FeCl_3$, $SnCl_4$ and $SbCl_5$ [74, 76].

The cleavage of alkyl ethers by acid anhydrides in the presence of BF_3 takes place with comparative difficulty but more easily than in the presence of chlorides of metals, and is not accompanied by such side reactions as the formation of acid fluoroanhydrides [76]. If equivalent quantities of ethyl ether, acetic anhydride and boron fluoride react for 15 hr at room temperature, ethyl acetate is obtained with 14·8 per cent yield, but if the duration of the reaction is 16·5 days the yield is 71·6 per cent. The cleavage of an ether by succinic and phthalic anhydrides takes place with more difficulty [76].

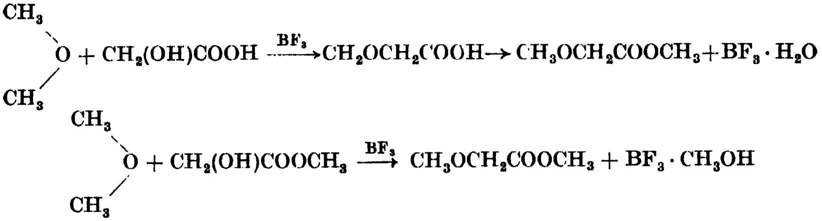
Carboxylic acids decompose alkyl ethers in the presence of boron fluoride at elevated temperatures. The cleavage as a whole may be represented by the following equations:

$$\mathrm{ROR + R'COOH \rightarrow R'COOR + ROH}$$
$$\mathrm{ROH + R'COOH \rightarrow R'COOR + H_2O}$$

If diethyl ether is heated for 3 hr in sealed tubes to 200° with acetic, propionic and cinnamic acids in the presence of $BF_3 . O(C_2H_5)_2$ the ethyl ester of the specified acids is obtained with yields of 47, 54 and 43 per cent respectively [77]. *n*-Butyl ether is decomposed by acetic acid in similar conditions with the formation of butyl acetate with a yield of 40 per cent. Di*iso*amyl ether with propionic and benzoic acids and $BF_3 . O(C_2H_5)_2$ gives *iso*amyl propionate and *iso*amyl benzoate with a yield of 32 and 21 per cent respectively.

S. V. Zavgorodnii [78] studied the reaction of boron fluoride ethyl etherate with acetic, chloroacetic and bromoacetic acids and found that in the given case the extent of the cleavage depends on the acid and increases from acetic to chloroacetic acid. Thus, boron fluoride ethyl etherate with acetic acid in 1 : 2 ratio gives ethyl acetate with 21 per cent yield on heating for 20 hr on a boiling water bath. Ethyl chloroacetate in similar conditions is formed with a yield of 32 per cent. When boron fluoride ethyl etherate is heated with bromoacetic acid in 1 : 2 ratio for 6 hr on an oil bath at a temperature of 135—145° ethyl bromoacetate is obtained with a yield of 52 per cent.

Alkyl ethers are split by hydroxycarboxylic acids [79] or their esters [80—82] in the presence of BF_3, and also of its complexes with ethers and water, with the formation of alkoxy acids or their esters. The cleavage of dimethyl ether by glycollic acid and its methyl ester may be represented by the scheme

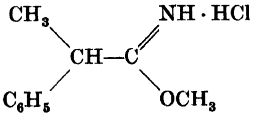


It is interesting to note that vinyl- and allylalkyl ethers are also split by carboxylic acids in the presence of boron fluoride ethyl etherate with the formation of alkyl esters of carboxylic acids [83].

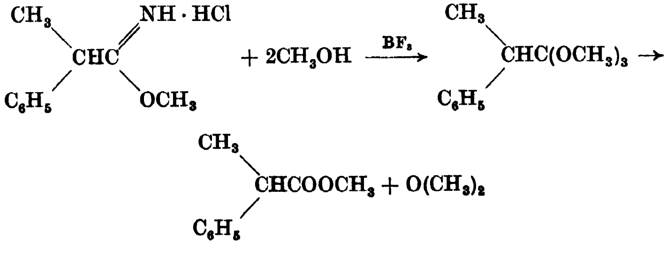
Alcoholysis of Esters

In a number of patents [84—86], it is recommended that boron fluoride be used, side by side with other catalysts, for the esterification of high aliphatic acids with alcohols. As original reagents it is not the free acids that are taken but oils and fats, and they are treated with a large excess of alcohol in the presence of BF_3 under pressure and at a temperature near the boiling point of the alcohol. In addition the oils and fats are saponified and the higher acids formed are esterified.

With mono- and dihydric phenols in the presence of boron fluoride dissolved in anisole at room temperature, β-penta-acetyl-D-glucose is converted into the corresponding phenyl-β-D-glucoside tetraacetate [87]. Imidoester hydrochlorides, for example methyl-α-phenyliminopropionate hydrochloride



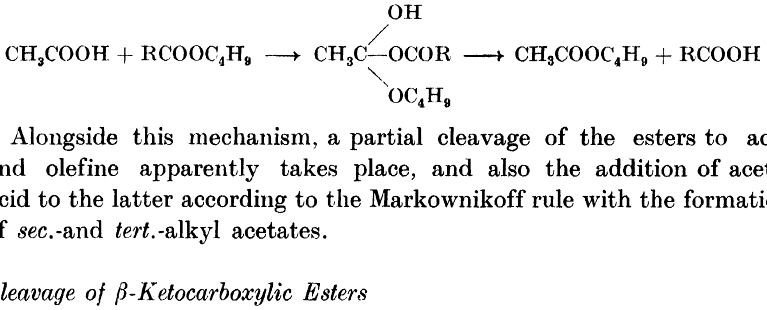
in benzene solution with absolute methyl alcohol and BF_3 forms methyl α-phenylpropionate with 85 per cent yield [88]. The conversion probably takes place through the formation of orthoesters according to the scheme



Acidolysis of Esters

On heating esters of formic, propionic, benzoic, salicylic and other acids to 100° with acetic acid in the presence of $BF_3 . 2CH_3COOH$ their acid residue is changed to acetyl and they are converted into acetates [89]. At the same time, esters with normal structure of alcohol residue form, besides the acetates with the same structure of the alcohol residue, small amounts of products of isostructure. For example, *n*-butyl formate is converted into *n*-butyl acetate and partially into *sec.*-butyl acetate. *n*-Butyl propionate forms *n*-butyl acetate with 43 per cent yield and *sec.*-butyl acetate with 4 per cent yield. *n*-Butyl benzoate gives *n*-butyl acetate with 69 per cent yield and *sec.*-butyl acetate with 5 per cent yield.

It is considered probable that the mechanism of this change by the acyl groups consists in the reaction of acetic acid with the esters and subsequent decomposition of the intermediate product formed into alkyl acetate and acid according to the scheme



$$CH_3COOH + RCOOC_4H_9 \longrightarrow CH_3\overset{OH}{\underset{OC_4H_9}{C}}{-}OCOR \longrightarrow CH_3COOC_4H_9 + RCOOH$$

Alongside this mechanism, a partial cleavage of the esters to acid and olefine apparently takes place, and also the addition of acetic acid to the latter according to the Markownikoff rule with the formation of *sec.*-and *tert.*-alkyl acetates.

Cleavage of β-Ketocarboxylic Esters

The cleavage of these esters by organic acids in the presence of BF_3 into esters and ketones takes place according to the equation [90] $R^1COCHR^2COOR^3 + R^4COOH \rightarrow R^1COCH_2R^2 + R^4COOR^3 + CO_2$ (R^1 is alkyl or alkoxyl; R^2 is alkyl, acyl or alkoxyl; R^3 and R^4 are alkyls.) This cleavage takes place very readily and is recommended for the preparation of *β*-diketones. Thus, methyl diacetylacetate with glacial acetic acid forms pentanedione-2,4 with 75 per cent yield.

Esters of the general formula $X(CH_2CH_2COOR)_2$ (X is O or S; R is an alkyl radical containing up to 18 carbon atoms) are decomposed in the presence of BF_3 giving acrylic esters [91]. If, for example, a diallyl ester of the structure $O(CH_2CH_2COOCH_2CH{=}CH_2)_2$ is heated to 200° with $BF_3 . O(C_2H_5)_2$ allyl acrylate is obtained according to the reaction

$$O(CH_2CH_2COCH_2CH = CH_2)_2 \rightarrow 2CH_2 = CHCOOCH_2CH = CH_2$$

An ester of similar structure $O(CH_2CH_2COOC_4H_9)_2$ is split up giving butyl acrylate. The yield of acrylates amounts to 60—70 per cent.

Reactions of Acid Amides and Nitriles

Acid amides and still more their boron fluoride coordination compounds split off ammonia as a boron fluoride coordination compound on reacting with alcohols, and form esters according to the reaction [92, 93]

$$\mathrm{RCONH_2 + R'OH \xrightarrow{BF_3} RCOOR' + BF_3 \,.\, NH_3}$$

Methyl-, ethyl-, *iso*propyl-, *n*-butyl-, *tert.*-butyl- and phenyl acetates are obtained by this method with a yield of 71, 62, 32, 50, 38 and 50 per cent respectively [92]. The boron fluoride from the complex $BF_3 . NH_3$, formed in the given reaction, may be recovered quantitatively by decomposing with sulphuric acid. One mole BF_3 per 1 mole amide is usually taken for this reaction, or the compounds $RCONH_2 . BF_3$ are previously prepared and then heated with alcohols or phenols.

Acid amides react unusually with organic acids in the presence of BF_3. By analogy with alcohols it was necessary to suppose that acid amides with organic acids and BF_3 would split off ammonia as $BF_3 . NH_3$ and form acid anhydrides. However, as the experimental investigations showed, the reaction in this case goes in the other direction. Instead of the expected acid anhydrides, the nitriles of the acids are obtained in almost theoretical yield [94]. Thus, if 1 mole acetamide, 0·5 mole acetic acid and 0·5 mole BF_3 are boiled for 30 min, acetonitrile is formed with a yield of 97 per cent. If 0·25 mole acetic acid is used the yield of acetonitrile amounts to 98 per cent. Other acids (propionic, butyric and benzoic) with acetamide give the nitrile with a yield of about 75—89 per cent (with benzoic acid the yield of nitrile is 20 per cent). If acetamide and BF_3 are heated without acids as in all the previous reactions, $BF_3 . NH_3$ separates out and acetonitrile is formed, but the yield of the latter does not exceed 15 per cent. It follows from this that the acids used in this reaction are not reagents but serve only as good activators for the catalyst.

When boron fluoride compounds of acid amides react with primary and secondary aliphatic and aromatic amines in the conditions described above, N-substituted acid amides are obtained according to the reaction

$$\mathrm{R'CONH_2 \,.\, BF_3 + HNR_2 \rightarrow R'CONR_2 + BF_3 \,.\, NH_3}$$

(R is aryl or alkyl).

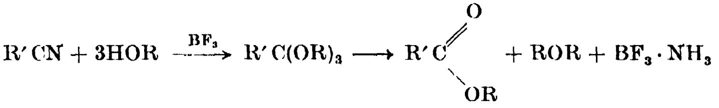
For a general presentation of the reactivity of the individual amides, the yields of N-substituted amides obtained by the method described are given in Table 84.

Nitriles of acids with alcohols in the presence of BF_3, like amides, form esters and ethers [95]. Acetonitrile, for example, with 3 moles of *n*-propyl alcohol in the presence of 1 mole BF_3, on boiling for 1 hr gives *n*-propyl acetate with 28 per cent yield and dipropyl ether with 27 per cent yield. With *n*-butyl alcohol in the same conditions, *n*-butyl acetate is obtained with 40 per cent yield and di-*n*-butyl ether with 38 per cent yield. Benzonitrile with *n*-propyl alcohol gives *n* -propyl benzoate (yield 30 per cent) and dipropyl ether (yield 26 per cent).

Table 84. Yield of N*-alkylamides obtained by the action of amines on amides in the presence of* BF_3

Amide	Amine	Compound obtained	Yield (%)
$CH_3CONH_2 . BF_3$	$n\text{-}C_4H_9NH_2$	$CH_3CONHC_4H_9$	37
$CH_3CONH_2 . BF_3$	$iso\text{-}C_5H_{11}NH_2$	$iso\text{-}C_5H_{11}NHCOCH_3$	64
$CH_3CONH_2 . BF_3$	$(iso\text{-}C_4H_9)_2NH$	$(iso\text{-}C_4H_9)_2NCOCH_3$	27
$CH_3CONH_2 . BF_3$	$C_6H_5NH_2$	$C_6H_5NHCOCH_3$	99
$CH_3CONH_2 . BF_3$	$C_6H_5NHCH_3$	$C_6H_5N(CH_3)COCH_3$	54
$CH_3CONH_2 . BF_3$	$\alpha\text{-}C_{10}H_7NH_2$	$\alpha\text{-}C_{10}H_7NHCOCH_3$	45
$CH_3CONH_2 . BF_3$	$\beta\text{-}C_{10}H_7NH_2$	$\beta\text{-}C_{10}H_7NHCOCH_3$	17
$CH_3CONH_2 . BF_3$	$C_6H_5NHC_2H_5$	$C_6H_5N(C_2H_5)COCH_3$	45
$CH_3CH_2CONH_2 . BF_3$	$C_6H_5NH_2$	$C_6H_5NHCOCH_2CH_3$	97
$C_6H_5CONH_2 . BF_3$	$C_6H_5NH_2$	$C_6H_5NHCOCH_3$	95

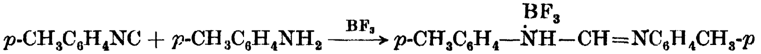
It is considered probable that the reactions described take place through the formation of ortho esters as intermediate products according to the scheme



$$R'CN + 3HOR \xrightarrow{BF_3} R'C(OR)_3 \longrightarrow R'C\begin{matrix}\nearrow O\\ \searrow OR\end{matrix} + ROR + BF_3 \cdot NH_3$$

The basis for the proposal of this mechanism is the capacity of ethyl orthoformate of decomposing in the presence of BF_3 into boron fluoride ethyl etherate and the boron fluoride compound of ethyl formate.

*iso*Nitriles and primary aromatic amines condense in the presence of BF_3 [96]. For *p*-tolyl*iso*nitrile and *p*-toluidine the reaction may be represented by the following equation:

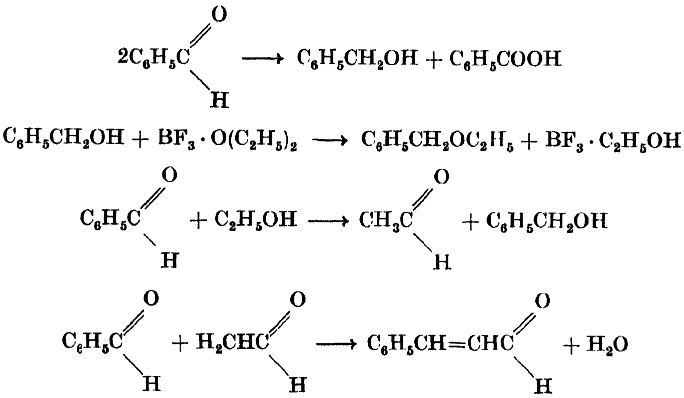


$$p\text{-}CH_3C_6H_4NC + p\text{-}CH_3C_6H_4NH_2 \xrightarrow{BF_3} p\text{-}CH_3C_6H_4\text{—}\overset{BF_3}{\dot{N}H}\text{—}CH{=}NC_6H_4CH_3\text{-}p$$

4. CONDENSATION OF ALDEHYDES

Aldehydes are capable of reacting with the most varied compounds having active hydrogen atoms, in the presence of a catalyst of boron fluoride and its complexes. Every reaction takes place at the expense of the aldehyde group by the usual aldol and crotonic condensation or by addition at the double bond of the carbonyl group.

Benzaldehyde (25 g), mixed with boron fluoride ethyl etherate (75 ml) at a temperature below 6° and left for 3 days in an ice bath gives cinnamic aldehyde (5·25 g) [97] and small quantities of ethyl benzyl ether [98]. It is considered probable that the formation of cinnamic aldehyde takes place through the following intermediate stages:



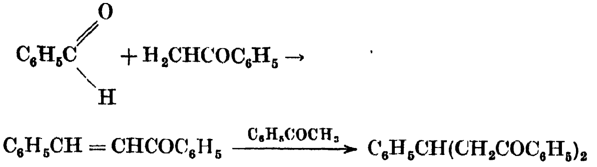
$$2C_6H_5CHO \longrightarrow C_6H_5CH_2OH + C_6H_5COOH$$

$$C_6H_5CH_2OH + BF_3\cdot O(C_2H_5)_2 \longrightarrow C_6H_5CH_2OC_2H_5 + BF_3\cdot C_2H_5OH$$

$$C_6H_5CHO + C_2H_5OH \longrightarrow CH_3CHO + C_6H_5CH_2OH$$

$$C_6H_5CHO + H_2CHCHO \longrightarrow C_6H_5CH{=}CHCHO + H_2O$$

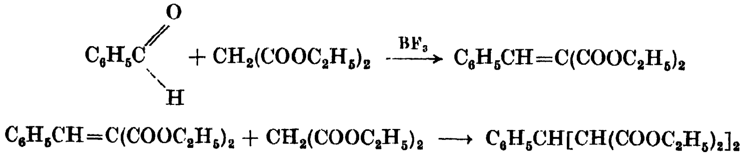
Benzaldehyde saturated with boron fluoride and cooled well readily condenses with acetophenone and forms benzalacetophenone with 66 per cent yield and a little benzylidenediacetophenone [99]:



$$C_6H_5CHO + H_2CHCOC_6H_5 \rightarrow$$

$$C_6H_5CH = CHCOC_6H_5 \xrightarrow{C_6H_5COCH_3} C_6H_5CH(CH_2COC_6H_5)_2$$

Malonic ester with benzaldehyde in the presence of boron fluoride first forms benzalmalonic ester (I) to which is then added a second molecule of malonic ester, and as a result benzaldimalonic ester (II) is obtained with a yield of 43·6 per cent:



$$C_6H_5CHO + CH_2(COOC_2H_5)_2 \xrightarrow{BF_3} C_6H_5CH{=}C(COOC_2H_5)_2 \qquad (I)$$

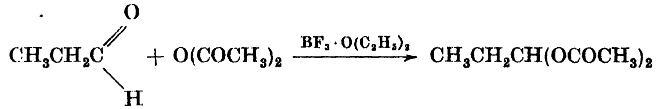
$$C_6H_5CH{=}C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 \longrightarrow C_6H_5CH[CH(COOC_2H_5)_2]_2 \qquad (II)$$

Aliphatic and aromatic aldehydes in the presence of catalytic quantities of boron fluoride ethyl etherate add acid anhydrides to their carbonyl group and form diethers of alkylidenes with a yield of 65—81 per cent [100], as seen from Table 85.

Table 85. *Condensation of aldehydes with acid anhydrides in the presence of* $BF_3 . O(C_2H_5)_2$

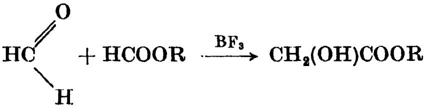
Reagent		Compound obtained	b. p. (°C/mm)	Yield (%)
Aldehyde	Anhydride			
Acetic	Acetic	Ethylidene diacetate	54—55/10	65
Propionic	Acetic	Propylidene diacetate	68·5—70/12	73
*iso*Butyric	Acetic	*iso*Butylidene diacetate	74—76/10	80
Benzoic	Acetic	Benzylidene diacetate	134·5/10	80
Propionic	Propionic	Propylidene dipropionate	110—111/10	73
Propionic	Butyric	Propylidene dibutyrate	88—88·5/10	71
Benzoic	Butyric	Benzylidene dibutyrate	160—162/3·5	81

For propionaldehyde and acetic anhydride the reaction may be represented by the following equation:



$$CH_3CH_2\underset{H}{\overset{O}{C}} + O(COCH_3)_2 \xrightarrow{BF_3 \cdot O(C_2H_5)_2} CH_3CH_2CH(OCOCH_3)_2$$

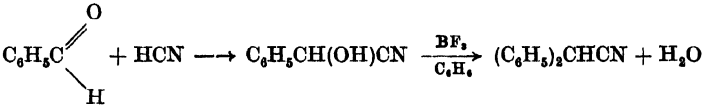
In the presence of free BF_3 benzaldehyde condenses with acetic anhydride as in the reaction with acetophenone with the formation of cinnamic acid [99]. Ethyl acetate, although it has mobile hydrogen α-atoms in the methyl group, does not enter into a similar condensation reaction with benzaldehyde saturated with boron fluoride at a temperature of 100° [99]. Esters of formic acid with formaldehyde give alkyl esters of glycollic acid according to the reaction



$$H\underset{H}{\overset{O}{C}} + HCOOR \xrightarrow{BF_3} CH_2(OH)COOR$$

Aldehydes are easily condensed with phenols in the presence of boron fluoride and its complexes at a temperature of 40—100°. At the same time, light transparent phenolaldehyde resins are obtained [101].

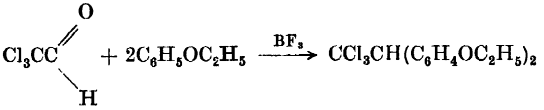
Formaldehyde with 2-alkylthiophenes or their chloroderivatives in the presence of BF_3 at a temperature above 200° gives alkenyl thiophenes [102]. When BF_3 (75 g) is passed into a mixture of benzaldehyde (106 g), hydrocyanic acid (35 g) and benzene (117 g) at such a rate that the temperature rises from 0° at the beginning of the experiment to 85° at the end, diphenylacetonitrile is obtained with a yield of 80 per cent [103]



$$C_6H_5\underset{H}{\overset{O}{C}} + HCN \longrightarrow C_6H_5CH(OH)CN \xrightarrow[C_6H_6]{BF_3} (C_6H_5)_2CHCN + H_2O$$

Boron fluoride is recommended as a catalyst for the condensation of acetyl derivatives of sugars with alcohols [104], glucose with the trimer of acetaldehyde [105], and also formaldehyde or its polymers with carbon monoxide [106], or with aliphatic nitrites [107] with the formation of glucosides, 4,6-ethylidene-D-glucopyranose, glycollic acid and methylene diamides respectively.

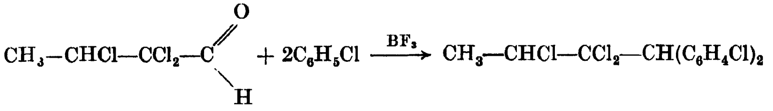
Those aldehydes which have such substituents as halogen in the α-position to the aldehyde group enter particularly vigorously into the reaction. Chloral, for example, with one molecule of aryl- or alkylphenyl ether in the presence of BF_3 forms, by the usual aldol condensation, 1-(alkoxy- or aryloxyphenyl)-2,2,2-trichloroethanol [108]. One molecule of chloral may be condensed with two molecules of alkylphenyl ethers giving 1,1-di-(4-alkoxyphenyl)-2,2,2-trichloroethane [109]. This reaction may be represented for phenetole by the following equation:



$$\mathrm{Cl_3C}\overset{\displaystyle O}{\underset{\displaystyle H}{C}} + 2\mathrm{C_6H_5OC_2H_5} \xrightarrow{BF_3} \mathrm{CCl_3CH(C_6H_4OC_2H_5)_2}$$

In just the same way chloroacetaldehyde condenses with excess of alkylphenyl ethers in the presence of BF_3 with the formation of 1,1-dialkoxyphenyl-2-chloroethanes [110], which, like DDT, have insecticidal properties.

α,α,β-Trihalobutyraldehydes and aromatic hydrocarbons or their derivatives (ethers, ketones, halogen-substituted derivatives) form compounds of the general formula $CH_3CHXCX_2CHAr_2$ (where Ar is aryl, containing a substituent among them, and X is halogen). As an example of this reaction may be quoted the formation of 1,1-di-(4-chlorophenyl)-2,2,3-trichlorobutane [111] from 2,2,3-trichlorobutyraldehyde and chlorobenzene according to the reaction



$$\mathrm{CH_3{-}CHCl{-}CCl_2{-}}\overset{\displaystyle O}{\underset{\displaystyle H}{C}} + 2\mathrm{C_6H_5Cl} \xrightarrow{BF_3} \mathrm{CH_3{-}CHCl{-}CCl_2{-}CH(C_6H_4Cl)_2}$$

Unsaturated haloaldehydes, for example $\mathrm{CCl_2=CClC}{\substack{\nearrow O\\ \searrow H}}$, $\mathrm{CBr_2=CBrC}{\substack{\nearrow O\\ \searrow H}}$ or their derivatives, condense in a similar way with one or two molecules of aromatic compounds (containing reactive hydrogen atoms) in the presence of boron fluoride [113]. For example, 2,3,3-trichloropropenal with two molecules of chlorobenzene gives 1,1-di-(4-chlorophenyl)-2,3,3-trichloropropene.

5. ACYLATION REACTIONS

Acylation of Ketones (Synthesis of β-Diketones)

The condensation of ketones with acid anhydrides in the presence of boron fluoride according to the equation

$$RCOCH_3 + (R'CO)_2O \xrightarrow{BF_3} RCOCH_2COR' + BF_3 \cdot R'COOH$$

has come into present day textbooks on organic chemistry as the classical method for the synthesis of β-diketones which are impossible to prepare by the Friedel—Crafts method [114]. It is carried out with ketones having the functional group—$COCH_2$—, by simple saturation of the ketone and acid anhydride mixture in 1 : 2 ratio with boron fluoride in the cold.

Hauser and Adams [115] studied the acetylation of three types of unsymmetrical aliphatic ketones by acetic anhydride in the presence of BF_3, each ketone being able to form two different monoacetyl derivatives:

$$\text{(I)} \quad CH_3COCH_2R + (CH_3CO)_2O \rightarrow CH_3COCH_2COCH_2R + CH_3COCHRCOCH_3$$

$$\text{(II)} \quad CH_3COCHR_2 + (CH_3CO)_2O \rightarrow CH_3COCH_2COCHR_2 + CH_3COCR_2COCH_3$$

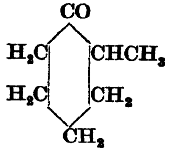
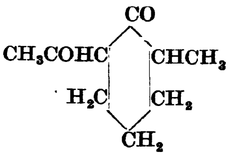
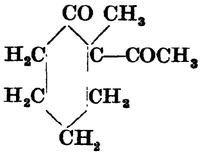
$$\text{(III)} \quad RCH_2COCHR_2 + (CH_3CO)_2O \rightarrow CH_3COCHRCOCHR_2 + CH_3COCR_2COCH_2R$$

As a result of the investigations it was found that in the sequence methyl-, ethyl-, methyl-*n*-propyl-, methyl*iso*butyl-, methyl-*n*-amyl-, methyl-*n*-hexyl-, methyl*iso*propyl ketone and 2-methyl*cyclo*hexanone higher yields of acetyl derivatives are obtained for methyl-*n*-amyl- and methyl-*n*-hexyl ketones. Considerable quantities of ketones (15—20 per cent) do not participate in the reaction and are recovered. High boiling products are partly obtained.

It is seen from Table 86 that methyl-*n*-alkyl ketones form mainly methylene derivatives and give very little of the methyl derivatives. Methyl*iso*butyl ketone, which has a branched structure, forms a little more methyl than methylene derivative, but methyl*iso*propyl ketone gives mainly methinyl derivatives besides the methyl derivative.

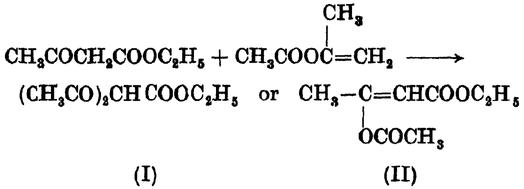
When acetic anhydride is condensed with acetone, diethylketone, *cyclo*hexanone, acetophenone, α-tetralone and ethyl acetate, there are obtained respectively acetylacetone, β-acetyldiethylketone (63 per cent), 2-acetyl*cyclo*hexanone (56 per cent), benzoylacetone (83 per cent), 2-acetyl-1-tetralone and acetoacetic ester [116] (the yield of product is given in brackets). Similarly *o*-, *m*- and *p*-nitroacetophenones are acetylated by acetic anhydride in the presence of BF_3 [111]. Ketones are acylated to β-diketones

Table 86. *Acetylation of aliphatic ketones in the presence of* BF_3

Acetylated ketone	Total yield (%)	Methyl derivatives of the ketones		Methylene derivatives of the ketones		Methinyl derivatives of the ketones	
		Formula	Relative yield (%)	Formula	Relative yield (%)	Formula	Relative yield (%)
$CH_3COCH_2CH_3$	32	—	—	$CH_3CH(COCH_3)_2$	100	—	—
$CH_3COCH_2CH_2CH_3$	34	$C_3H_7COCH_2COCH_3$	10	$C_2H_5CH(COCH_3)_2$	90	—	—
$CH_3COCH_2CH(CH_3)_2$	41	*iso*-$C_4H_9COCH_2COCH_3$	55	*iso*-$C_3H_7CH(COCH_3)_2$	45	—	—
$CH_3CO(CH_2)_4CH_3$	59	$C_5H_{11}COCH_2COCH_3$	10	$C_4H_9CH(COCH_3)_2$	90	—	—
$CH_3CO(CH_2)_5CH_3$	53	$C_6H_{13}COCH_2COCH_3$	10	$C_5H_{11}CH(COCH_3)_2$	90	—	—
$CH_3COCH(CH_3)_2$	28	$(CH_3)_2CHCOCH_2COCH_3$	32	—	—	$(CH_3)_2C(COCH_3)_2$	68
	35	—	—		50		50

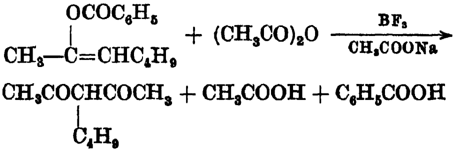
in the presence of boron fluoride and by other anhydrides of aliphatic acids, for example, propionic, butyric, *iso*butyric and *n*-caproic [117].

Alkyl esters of ketocarboxylic acids, particularly ethyl acetoacetate, are acetylated by *iso*propenyl acetate in the presence of $BF_3 . O(C_2H_5)_2$ not at the hydrogens of the methyl group linked to the ketonic group, but by the substitution, depending on the ratios of the reagents, of the hydrogen of the methylene group or the hydrogen of the hydroxyl group of the enol form of the ester, by acetyl [118]. When ethyl acetoacetate and *iso*propenyl acetate are used in equimolecular proportions, the C-acetyl derivative (I) is formed; if 0·5 mole ethyl acetoacetate is taken for 1 mole *iso*propenyl acetate, the O-acetyl derivative of acetoacetic ester (II) is obtained with the separation of acetone in both cases:



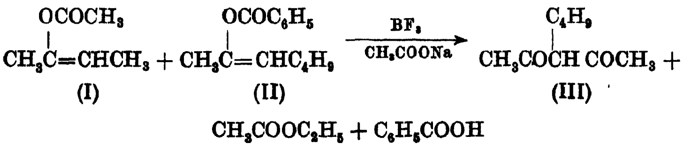
$$CH_3COCH_2COOC_2H_5 + CH_3COO\overset{CH_3}{\overset{|}{C}}{=}CH_2 \longrightarrow$$
$$\underset{(I)}{(CH_3CO)_2CH\,COOC_2H_5} \quad \text{or} \quad \underset{(II)}{CH_3-\underset{OCOCH_3}{\underset{|}{C}}{=}CHCOOC_2H_5}$$

Keto-enol esters of carboxylic acids are also acylated by acid anhydrides or chloroanhydrides in the presence of BF_3 with the formation of β-diketones [119]. For the enolbenzoate of methyl-*n*-amyl ketone with acetic anhydride the reaction may be represented in the following way:



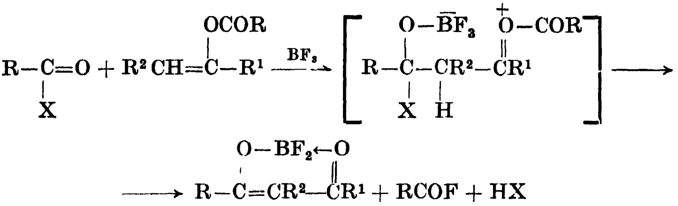
$$CH_3-\overset{OCOC_6H_5}{\overset{|}{C}}{=}CHC_4H_9 + (CH_3CO)_2O \xrightarrow[CH_3COONa]{BF_3}$$
$$CH_3CO\underset{C_4H_9}{\underset{|}{C}}HCOCH_3 + CH_3COOH + C_6H_5COOH$$

When keto-enol esters are heated with BF_3 and sodium acetate they undergo autoacylation to β-diketones. Autoacylation may occur between two molecules of one or different esters. The enolacetate of methylethyl ketone (I) and the enolbenzoate of methyl-*n*-amylketone (II) form 3-*n*-butylpentanedione-2,4 (III) according to the reaction



$$\underset{(I)}{CH_3\overset{OCOCH_3}{\overset{|}{C}}{=}CHCH_3} + \underset{(II)}{CH_3\overset{OCOC_6H_5}{\overset{|}{C}}{=}CHC_4H_9} \xrightarrow[CH_3COONa]{BF_3} \underset{(III)}{CH_3CO\overset{C_4H_9}{\overset{|}{C}}H\,COCH_3} +$$
$$CH_3COOC_2H_5 + C_6H_5COOH$$

It is considered probable that the initial stages of the condensations described are the formation of a boron fluoride complex of the β-diketone, which when treated with a solution of sodium acetate decomposes on heating into the diketone and the fluoroanhydride of the carboxylic acid according to the scheme



$$R-\underset{X}{\underset{|}{C}}=O + R^2CH=\overset{OCOR}{\overset{|}{C}}-R^1 \xrightarrow{BF_3} \left[R-\underset{X}{\underset{|}{\overset{O-\bar{B}F_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{CR^2}}-\overset{\overset{+}{O}-COR}{\overset{\|}{C}R^1} \right] \longrightarrow$$

$$\longrightarrow R-\overset{O-BF_2\leftarrow O}{C=CR^2-CR^1} + RCOF + HX$$

[X=OCR¹=CHR² or OCOR]

The intermediate boron fluoride complex described above was isolated in the autoacylation of the enolacetate of methyl*iso*butyl ketone. The fluoroanhydride of benzoic acid is formed in the autoacylation of the enolbenzoate of acetone and methyl-*n*-amylketone [119].

For some characteristics of the influence of the structure of ketones and acid anhydrides on the reaction, the yields of β-diketones obtained by the acylation of different ketones are given in Table 87.

Thus, the acylation of ketones is a general, simple and convenient method of preparing β-diketones. The boron fluoride method of acylation of ketones enables β-diketones to be synthesized, which are very difficult to obtain in good yield by the usual methods.

In some cases acylation in the presence of bases gives higher yields of β-diketones. Thus, in the acylation of acetophenone by butyric anhydride in the presence of sodamide the acyl derivative is obtained with 42 per cent yield, and in the presence of BF_3 with 15 per cent yield. The acylation of *cyclo*hexanone with propionic and butyric anhydrides in the presence of BF_3, however, gives the corresponding diketones with 35 per cent yield, but in the presence of bases, with 4—12 per cent yield.

In the acylation of methyl methylene ketones having α- and α'-active hydrogen atoms, the boron fluoride and the basic methods give different β-diketones. Methylbenzyl-, methylethyl- and higher methyl-*n*-alkyl ketones form methylene derivatives (I) with boron fluoride, but with bases they form methyl derivatives (II):

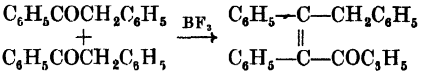
$$RCOX + CH_3COCH_2R' \xrightarrow[X=RCOO]{BF_3} RCOCHRCOCH_3 \qquad (I)$$

$$RCOX + CH_3COCH_2R' \xrightarrow[base]{X=OC_2H_5} RCOCH_2COCH_2R' \qquad (II)$$

The boron fluoride method is particularly important for the acylation of methylbenzyl ketone, because such β-diketones as α-phenylacetylacetone are difficult to synthesize by other methods [117].

In the presence of ketones with a reactive methylene group alongside the carbonyl group they can react together and give unsaturated ketones.

For example, phenylbenzyl ketone in the presence of BF_3 is converted into 1,2,3,4-tetraphenylbuten-2-one-1 [116] according to the reaction



$$\begin{array}{c}C_6H_5COCH_2C_6H_5\\ +\\ C_6H_5COCH_2C_6H_5\end{array}\xrightarrow{BF_3}\begin{array}{l}C_6H_5-C-CH_2C_6H_5\\ \qquad\;\;\|\\ C_6H_5-C-COC_3H_5\end{array}$$

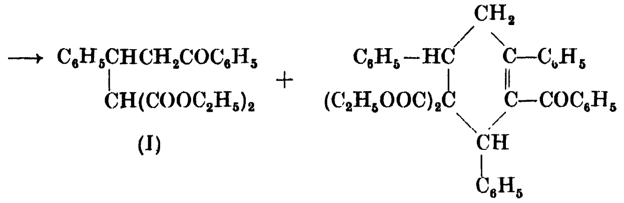
Unsaturated ketones with acetic anhydride in the presence of boron fluoride form unsaturated *β*-diketones with a lower yield than in the acylation of saturated ketones.

Table 87. *Acylation of ketones with acid anhydrides in the presence of* BF_3

Ketone	Anhydride	*β*-Diketone	Yield (%)
Acetone	Acetic	Acetylacetone	80—86
Acetone	Propionic	Propionylacetone	46
Acetone	*n*-Butyric	Butyrylacetone	48
*cyclo*Hexanone	Acetic	2-Acetyl*cyclo*hexanone	35
*cyclo*Hexanone	Propionic	2-Propionyl*cyclo*hexanone	35
*cyclo*Hexanone	*n*-Butyric	2-Butyryl*cyclo*hexanone	34
Acetophenone	Acetic	*ω*-Acetylacetophenone	50
Acetophenone	Propionic	*ω*-Propionylacetophenone	30
Acetophenone	*n*-Butyric	*ω*-Butyrylacetophenone	15
Methyl-*tert*.-butyl ketone	Acetic	2,2-Dimethylhexanedione-3,5	45
Diethyl ketone	*n*-Butyric	Methylpropionylbutyrylketone	46
Diethyl ketone	Acetic	3-Methylhexanedione-3,4	62·5
Di*iso*butyl ketone	Acetic	*iso*Propyl*iso*butyrylacetone	45
Methylethylketone	Acetic	Methylacetylacetone	32
Methylethylketone	Propionic	Methylpropionylacetone	31
Methylethylketone	*n*-Butyric	Methylbutyrylacetone	44
Methylethylketone	*n*-Caproic	Methylcaproylacetone	64
Methyl-*n*-amylketone	Acetic	*n*-Butylacetylacetone	53
		n-Hexoylacetone	6
Methyl-*n*-amylketone	Propionic	*n*-Butylpropionylacetone	47
		n-Propionyl-*n*-hexoylmethane	4
Methyl-*n*-amylketone	*n*-Butyric	*n*-Butylbutyrylacetone	38
		n-Butyryl-*n*-hexoylmethane	4
Methyl-*n*-amylketone	*iso*Butyric	*n*-Butyl*iso*butyrylacetone	29
		*iso*Butyryl-*n*-hexoylacetone	3
Methyl*iso*butylketone	Acetic	*iso*Valerylacetone	25
		*iso*Propylacetylacetone	16
Metyl*iso*butylketone	Propionic	Propionyl*iso*valerylmethane	26
		*iso*Propylpropionylacetone	17
Methyl*iso*butylketone	*n*-Butyric	Butyryl*iso*valerylmethane	26
		*iso*Propylbutyrylacetone	18
Methylbenzylketone	Acetic	3-Phenylacetylacetone	41

Unsaturated ketones in the presence of BF_3 can enter into reaction with compounds having reactive methylene groups, and can give products of addition at the double bond. The addition of malonic ester to benzalacetophenone with the formation of 1-benzoyl-2-phenylpropane-3,3-dicarboxylic ester (I) and small quantities of 1,3,5-triphenyl-2-benzoyl-4,4-dicarbethoxy*cyclo*hexene (II) may be quoted as an example of this reaction [99]:

$$C_6H_5CH{=}CHCOC_6H_5 + CH_2(COOC_2H_5)_2 \xrightarrow{BF_3}$$

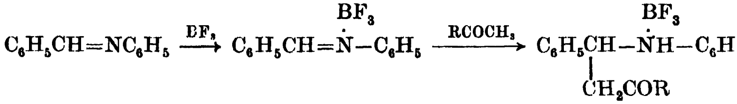


$$\longrightarrow \begin{array}{l} C_6H_5CHCH_2COC_6H_5 \\ | \\ CH(COOC_2H_5)_2 \end{array} + \text{(II)}$$

(I)

(II)

If we observe the interesting reaction of methyl ketones with benzin the presence of BF_3, which was studied by Snyder, Kornberg and Romig [120] it is a simple method of preparing β-aminoketones. As the authors found, if $BF_3 \,.\, O(C_2H_5)_2$ is added to a solution of benzalaniline in excess of ketone and the mixture is heated for a few minutes, the boron fluoride reacts vigorously with the benzalaniline and forms a coordination compound in which the double bond is so strongly polarized that it adds methyl ketones very easily and forms the corresponding aminoketones:



$$C_6H_5CH{=}NC_6H_5 \xrightarrow{BF_3} C_6H_5CH{=}\overset{BF_3}{\dot{N}}{-}C_6H_5 \xrightarrow{RCOCH_3} \begin{array}{l} C_6H_5CH{-}\overset{BF_3}{\dot{N}H}{-}C_6H_5 \\ \;| \\ CH_2COR \end{array}$$

According to this scheme, acetone, methyl ethyl ketone, methyl*iso*-butyl ketone, methyl-*n*-amylketone, pinacolone, benzylacetone, *cyclo*-pentanone, acetophenone and other ketones readily condense with benzalaniline.

The reaction may be carried out by first preparing the boron fluoride compound of benzalaniline and then mixing it with the ketone.

Ketimines are acetylated by acetic anhydride in the presence of boron fluoride [121]. N-(1,3-dimethylbutyl)-methyl*iso*butylketimine with acetic anhydride forms N-(1,3-dimethylbutyl)-acetonyl*iso*butylketimine, which is converted by subsequent hydrolysis into *iso*valerylacetone.

There are indications that cellulose [122] and hemimethoxylignin sulphate [123] are acetylated in the presence of BF_3. Aliphatic-aromatic ketones are converted by sulphur halides into high molecular compounds containing sulphur [124].

Recently an original synthesis of α-alkoxyketones, based on the decomposition of α-diazoketones with the help of boron fluoride ethyl etherate in the presence of alcohols, has been worked out [125]. If, for example, 5 g diazoacetophenone in 10 ml ethyl alcohol and 100 ml ether is treated with 0·2 g boron fluoride ethyl etherate at 25°, *a*-ethoxyacetophenone is obtained with 82 per cent yield. The reaction may be represented thus:

$$C_6H_5COCH_2N_2X + C_2H_5OH \xrightarrow{BF_3 \cdot O(C_2H_5)_2} C_6H_5COCH_2OC_2H_5 + N_2 + HX$$

By this method *a-iso*propoxyacetophenone, *tert.*-butoxyacetophenone and other alkoxyketones are prepared.

The Acylation of Aromatic Hydrocarbons and their Derivatives

Aromatic hydrocarbons, phenols and their ethers and heterocyclic compounds are acylated by means of haloanhydrides, anhydrides and carboxylic acids. In these reactions boron fluoride often acts in the same way as $AlCl_3$, and sometimes excels it or meets it halfway in catalytic effect.

(a) *Acylation of aromatic hydrocarbons by acid anhydrides.* The acetylation of aromatic hydrocarbons by acetic anhydride in the presence of boron fluoride was first studied by Meerwein and Vossen in 1934 [116]. To carry out the acetylation BF_3 was passed into a mixture of the hydrocarbon and acetic anhydride at 0° to saturation, the mixture was gradually heated until the BF_3 was completely removed, the reaction products were poured into an aqueous solution of sodium acetate, distilled in steam and treated with ether, and the extract was washed with a solution of sodium bicarbonate, dried with sodium sulphate and distilled. By this method acetophenone and *p*-methylacetophenone were obtained from benzene and toluene with a yield of 13·7 and 70·9 per cent respectively.

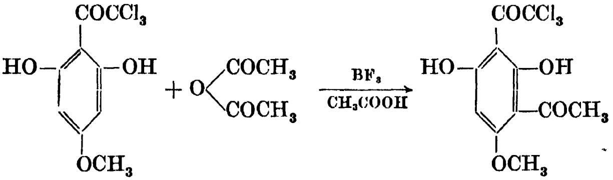
It is characteristic that *cyclo*hexene in this reaction also behaves like benzene but not as an olefine, and in the reaction with acetic anhydride tetrahydroacetophenone is obtained as final product with a yield of 27 per cent [116].

Solvents with a high dielectric constant exert a positive influence on the acylation of aromatic hydrocarbons with acid anhydrides. Thus, if a mixture of naphthalene and benzoic anhydride is saturated with excess of boron fluoride in nitrobenzene solution, after allowing the mixture to stand for 18—20 hr phenylnaphthyl ketone is obtained with 77 per cent yield, but in CCl_4 solution it is obtained with 4 per cent yield [126]. It is interesting that in both cases only phenyl-1-naphthyl ketone is formed. We may remember that when naphthalene is benzylated with benzyl alcohol in the presence of BF_3 it is also mainly *a*-benzylnaphthalene that is obtained [127]. This makes the boron fluoride synthesis of naphthyl ketones have a more promising future in comparison with the Friedel—Crafts reaction with benzoyl chloride and $AlCl_3$, which leads to the formation of a product containing the β-isomer, requires three times as long and gives a smaller yield of product [128].

(b) *Acylation of phenols and alkylphenyl ethers by acid anhydrides.* Phenols and alkylphenyl ethers are acylated by acid anhydrides more easily than aromatic hydrocarbons. If 0·75 mole phthalic anhydride and 1·5 moles phenol are heated for 1 hr with 50 g BF_3 phenolphthalein is obtained with 72 per cent yield, but if 50 g resorcinol and 60 g phthalic anhydride are boiled under a reflux condenser for 3 hr in the presence of 8 g BF_3 in 100 ml benzene, fluorescein is obtained in almost quantitative yield [95].

Resorcinol and acetic anhydride in ethyl ether, saturated at 0° with boron fluoride, give 2,6-dihydroxyacetophenone with a yield of 91 per cent of pure recrystallized product [129]. In the given case the boron fluoride method is appreciably simpler than the "zinc chloride method" used in organic synthesis [130], because it does not require vacuum distillation which is not suitable for the separation of high melting compounds, and it also permits resacetophenone to be obtained purer and with higher yield (the "zinc chloride method" gives a coloured product with 65 per cent yield).

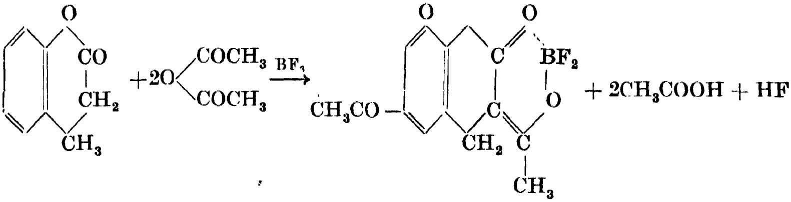
6-Methoxy-2,4-dihydroxymethyl benzoate and acetic anhydride in acetic acid, saturated with boron fluoride, form 3-acetyl-2,4-dihydroxy-6-methoxymethyl benzoate [131]. 4-Methoxy-2,6-dihydroxytrichloracetophenone with acetic anhydride and BF_3 is converted into 2,6-dihydroxy-4-methoxy-3-acetyltrichloracetophenone. The latter reaction may be represented in the following way :



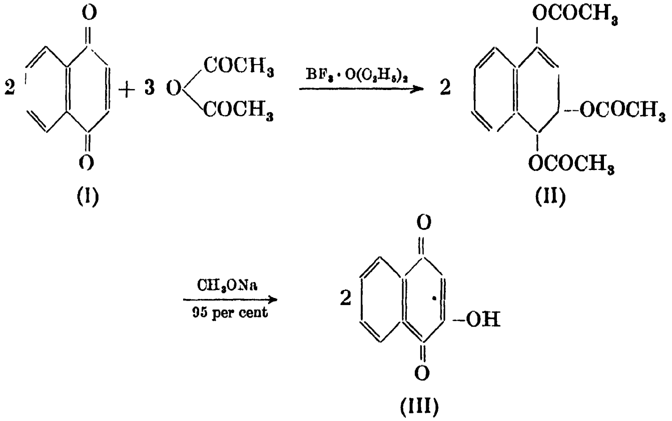
Alkyl ethers of phenols are acylated in a similar way by acid anhydrides. Anisole with acetic anhydride in the presence of BF_3 forms *p*-methoxyacetophenone with a yield of 95 per cent [116].

2-Naphthylmethyl ether and benzoic anhydride in nitrobenzene solvent, saturated with excess of boron fluoride, give phenyl-2-hydroxy-1-naphthyl ketone, which is completely soluble in a hot solution of caustic soda, with a yield of 70 per cent [126]. Consequently in the given case, hydrolysis of the ether takes place quantitatively alongside the benzoylation.

3,4-Dihydrocoumarin is acetylated by acetic anhydride on saturating with boron fluoride, in such a way that one acetyl group enters the benzene ring and the other enters the lactone ring. As a result 3,6-diacetohydrocoumarin is obtained with 40·6 per cent yield, which comes out as a very stable intramolecular boron fluoride compound [132]:



(c) *Acylation of quinones by acid anhydrides.* Boron fluoride as a complex with ethyl ether is a highly active catalyst in the reaction of quinones with acid anhydrides. Its use has made available substances such as 2-hydroxy-1,4-naphthoquinone (III) and its derivatives, which are of great significance for some special syntheses. On treating a mixture of α-naphthoquinone (I) and acetic anhydride with boron fluoride ethyl etherate the reaction proceeds in such a way that three acetyl groups enter into the quinone ring: two add to the oxygen atoms, and one (acetoxy) is directed to the β-position of the same ring. As a result 1,2,4-triacetoxynaphthalene (II) [133] is obtained in almost quantitative yield (81 per cent), and with sodium methylate in methanol this may be converted into 2-hydroxy-1,4-naphthoquinone (III):



Similarly 1,2,4-triacetoxy-5,8-dihydronaphthalene is obtained from 5,8-dihydronaphthoquinone.

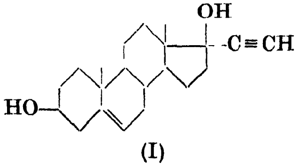
2-Phenyl-1,4-benzoquinone and acetic anhydride with $BF_3 . O(C_2H_5)_2$, heated for a few minutes and left for 1 hr at room temperature, give 2,5,?-triacetoxydiphenyl with 57 per cent yield (the position of the third acetoxy group has not been determined). On hydrolysis and oxidation this compound is converted into ?-hydroxy-2-phenyl-1,4-benzoquinone, which with acetic anhydride and $BF_3 . O(C_2H_5)_2$ forms the acetate at the expense of the hydroxyl group, but with methyl and amyl alcohols in $BF_3 . O(C_2H_5)_2$ is converted into the methyl and corresponding amyl ethers.

2-Acyl-1,4-naphthoquinone is acetylated by acetic anhydride in the presence of $BF_3 . O(C_2H_5)_2$ with the formation of 2-acyl-3,4-diacetoxy-1-naphthol fluoroborate [134], which is decomposed on boiling with 90 per cent ethyl alcohol to 2-acyl-3,4-diacetoxy-1-naphthol.

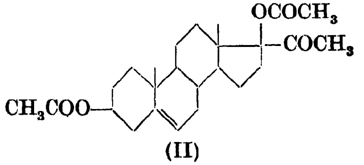
Dimethylaniline is not acylated by acid anhydrides, just as it is not alkylated by olefines in the presence of BF_3 on account of the great tendency of the catalyst to form stable inactive boronfluoride—dimethylaniline complexes [116].

The Acetylation of Steroids with Acetic Anhydride and Acetic Acid in the Presence of $BF_3 . O(C_2H_5)_2$ *and* HgO

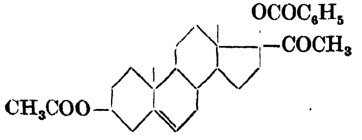
The efficiency of boron fluoride ethyl etherate as a catalyst in the acetylation of steroids containing hydroxyl groups which are difficult to esterify was demonstrated by Ruzicka *et al.* as early as 1938. It was found that when a mixture of HgO, $BF_3 . O(C_2H_5)_2$ and $O(COCH_3)_2$ is reacted with Δ^5-17-ethinylandrosten-3-*trans*-17α-diol (I) in glacial acetic acid, after suitable treatment Δ^5-3-*trans*-17α-diacetoxypregnen-20-one (II) is obtained [135—138]. Δ^5-17-Ethinyl-3-*trans*-17α-dihydroxyandrosten-3-acetate-17-benzoate is converted by the same method into Δ^5-3-*trans*-17-α-dihydroxypregnen-20-one-3-acetate-17-benzoate (III) [136], and Δ^5-17-ethinylandrostendiol-3β-acetate-17α-stearate into Δ^5-pregnen-20-one-diol-3β-acetate-17α-stearate (IV) [139].



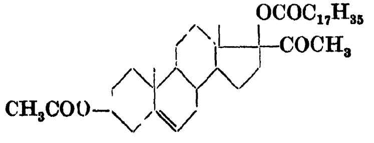
(I)



(II)

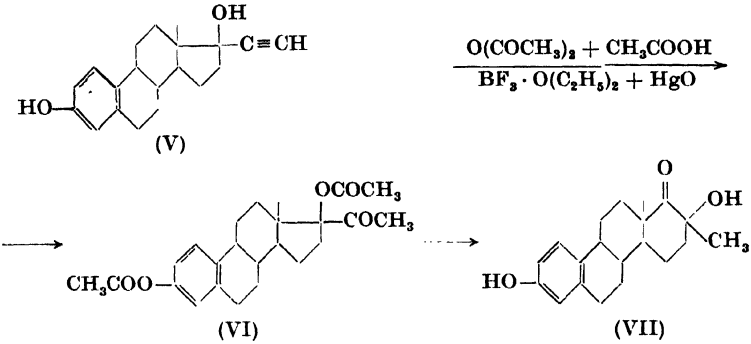


(III)



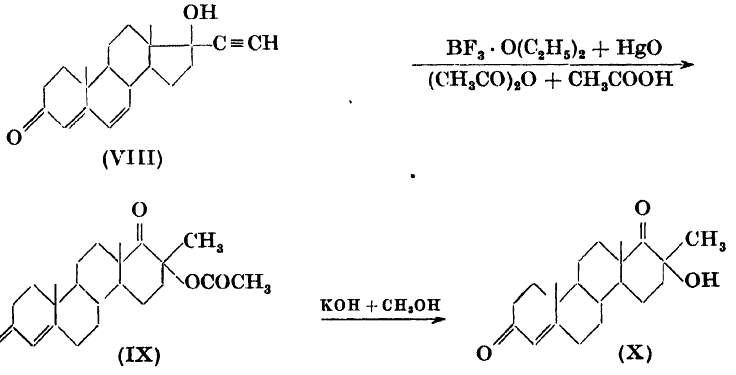
(IV)

In the given case the reaction proceeds in such a way that alongside the acetylation of the hydroxyl groups, the addition of acetic acid at the acetylenic bond probably takes place with the formation of a vinyl acetate derivative and its conversion to a ketonic derivative. When the reaction products are treated with alcoholic alkali the five-membered ring is probably enlarged to a six-membered one with the migration of the ketonic group into the ring. Therefore the carbon skeleton of the final product of the ketone is different from that in the original ethinylandrostendiol [137, 140]. Thus, 17-ethinyloestranediol (V) is acetylated by this method with the formation of a dihydroxyketone with a carbon skeleton other than that of the original steroid, which is seen from the following scheme:



(V) (VI) (VII)

If 17-ethinyltestosterone (VIII) (450 mg) in acetic acid (20 ml), is treated with $(CH_3CO)_2O$ (3 ml), HgO (450 mg) and $BF_3 . O(C_2H_5)_2$ (0·3 ml) and left for 15 hr at 20°, it gives the acetate of the diketone (IX) [137, 141], which on boiling with KOH, — CH_3OH is hydrolysed to the corresponding hydroxydiketone (X).

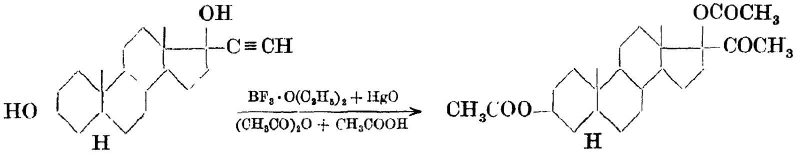


(VIII) (IX) (X)

In the same way 3β-acetoxypregnadien-5,16-one-20 is converted into 3β-acetoxypregnadien-5,16-one-20 [142].

Taking into account the great similarity of some of the products obtained by the described method to products separated from the suprarenal glands, Ruzicka *et al.* [143] extended this method of acetylation and the succession of reactions to the synthesis of compounds of the androstene series with positions 5 and 6 saturated.

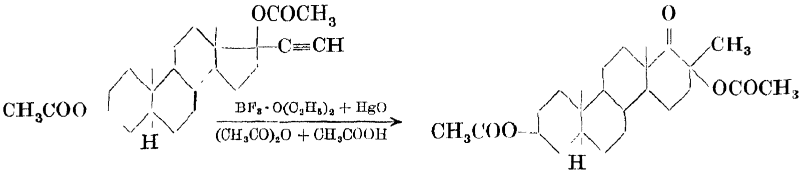
It was found that 17-ethinylandrostane-3-*trans*-17α-diol (XI) on acetylation forms the product (XII), identical with the product separated from the suprarenal glands, or differs from it only in the stereoisomerism at the C_{17}:



(XI) (XII)

If 17-ethinyl-3-*trans*-17α-dihydroxyandrostane-3-monoacetate (2 g) in 40 ml glacial CH_3COOH with $(CH_3CO)_2O$ (5 ml), HgO (1 g) and $BF_3 . O(C_2H_5)_2$ (0·6 ml) is left for 16 hr at room temperature it forms two acetates: with m. p. 222—224° (needles) and with m. p. 228—230° (plates).

In the same way 17-ethinyl-3-*trans*-17α-diacetoxyandrostane (XIII) gives, after 2 days standing, the diacetate of the dihydroxyketone with m.p. 228—230°. Probably also in this case the acetylation is accompanied by the rearrangement of the five-membered ring to a six-membered one with the formation of 1-chrysenonehexadecahydro-2,8-dihydroxy-2,10a-12a-trimethyldiacetate (XIV) [137].



(XIII) (XIV)

The presence of the described isomerization of the five-membered ring to a six-membered one in the acetylation process was later confirmed by a number of other investigations. It was found, for example, that 3β,17α-dihydroxypregnyne-20 (XVI) in acetic acid with $(CH_3CO)_2O$, HgO and $BF_3 . O(C_2H_5)_2$ forms 3β,17α-diacetoxypregnanone-20 (XVII). But on reacting the same compound with aniline, $BF_3 . O(C_2H_5)_2$ and $HgCl_2$ 3β-acetoxy-17α-hydroxypregnanone-20 (XVIII) is obtained, which differs from the previous compound by one acetyl group [144].

However, if (XVII) is formed through the enol acetate as noted above, the process of formation of (XVIII) goes via the formation of an anil [145], which is obtained by the addition of aniline to the acetylenic bond. The possibility of this addition is described in the literature in the reaction of heptyne-1 with aniline in the presence of the same catalyst [146].

When caustic alkali acts on the acetylation products they are hydrolysed and at the same time the five-membered rings are widened at the expense of the ketonic group into six-membered rings with the ketonic group in the ring.

Moreover, from (XVII) 3β,17a(α)-dihydroxy-17a-methyl-D-homoaetiocholanone-17 (XIX) is formed, but from (XVIII) 3β,17a(β)-dihydroxy-17a-methyl-D-homoaetiocholanone-17 (XX) is obtained, i.e. the compounds differ only in the stereoisomerism at the C_{17}. Subsequent acetylation of compounds (XIX) and (XX) or their monoacetyl derivatives [147] in a medium of CH_3COOH, $(CH_3CO)_2O$, HgO and $BF_3 . O(C_2H_5)_2$ gives the corresponding diacetyl derivatives of the same structure as the original compounds (XXI and XXII). All these changes are represented in the scheme below.

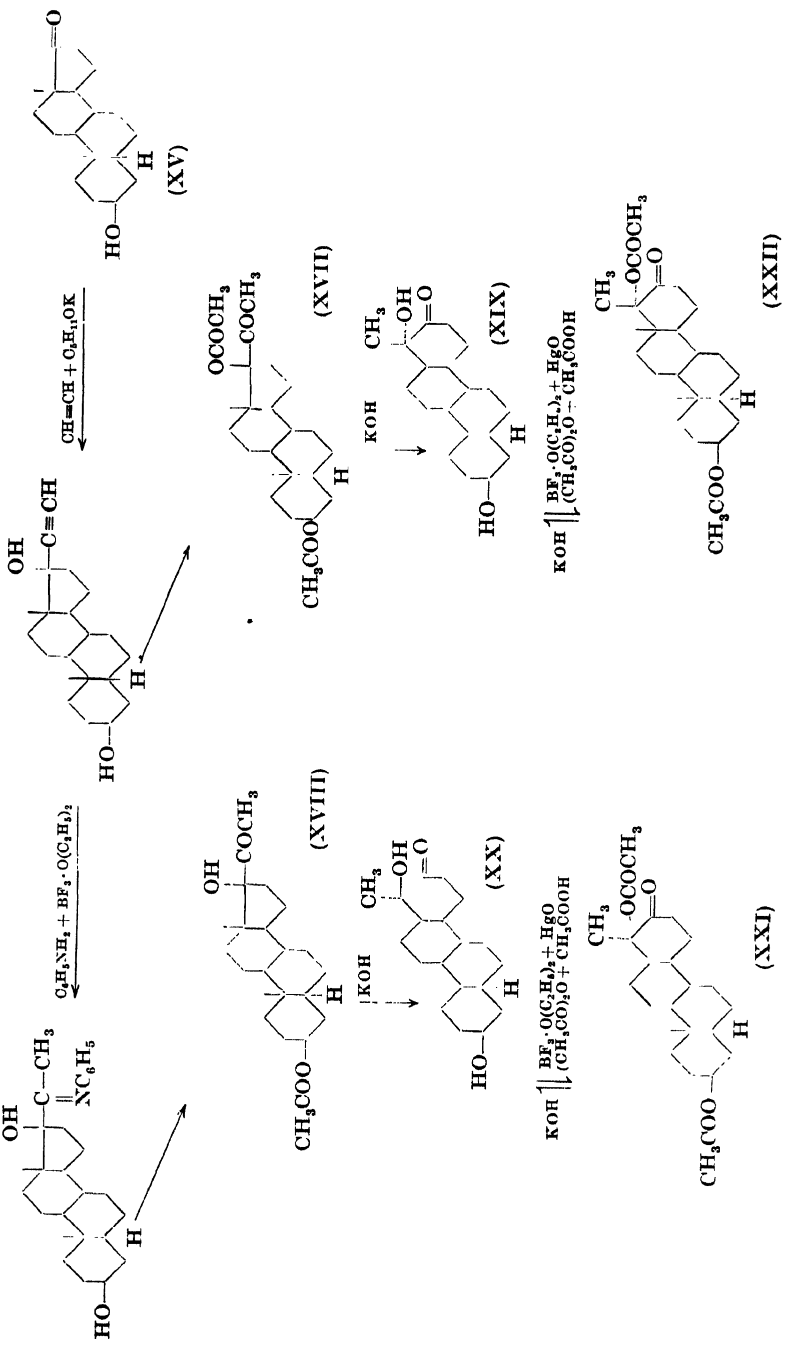
3β,17α-Dihydroxypregnen-5-one-20 undergoes a similar type of conversion on acetylation in the presence of $BF_3 . O(C_2H_5)_2$ and HgO [148].

Acylation of Heterocyclic Compounds by Acid Anhydrides

The first investigations on the use of boron fluoride as catalyst for the acylation of furan, thiophene and their derivatives appeared in 1947. In spite of the comparatively short time, the part played by BF_3 in these reactions has already been explained in sufficient detail. Boron fluoride may be used independently, but better as a coordination compound with acetic or orthophosphoric acids, methyl alcohol and particularly with ethyl ether. Also, in contrast to the alkylation of aromatic hydrocarbons, where this catalyst may be used in quantities of 1 mole or more to 1 mole hydrocarbon for the acylation of furan, thiophene and substituted furans and thiophenes with a good yield of the corresponding ketone, it is sufficient to introduce 0·001—0·1 mole BF_3 per 1 mole of acylated compound.

It is appropriate to note that this catalyst, like $AlCl_3$, in similar concentrations does not in general permit the acylation of furan and thiophene, and its use in large quantities (1 mole or more) gives comparatively low yields of ketonization products (up to 35 per cent).

Scheme of conversion of 3β, 17α-dihydroxypregnyne-20 [144]



Some idea of the activity of boron fluoride and its compounds in acylation reactions with acid anhydrides in comparison with other catalysts may be obtained from Table 88, from which it is seen that results approximately the same as with BF_3 may be obtained only with two catalysts: $FeCl_3$ and $H_2PO_3F.H_2O$.

The acylation of furan and thiophene usually takes place with the formation of a single compound, the 2-acyl derivative [149, 150] and thiophene alone with acetic anhydride gives two isomeric products: the 3- and 2-acetyl derivatives, with a predominance of the first [151]. In the acetylation of 2-acetylthiophene (0·33 mole) with acetic anhydride (1 mole) in the presence of large quantities of $BF_3 . O(C_2H_5)_2$ (0·84 mole) at 55° the second acetyl group does not enter into the heterocyclic ring, but the usual acetylation of the side chain, similar to the acetylation of acetophenone, takes place. As a result 2-triacetylthiophene is obtained with a yield of 17 per cent.

Free boron fluoride is probably a sufficiently stable catalyst for this reaction.

In the literature only the benzoylation of thiophene with benzoic anhydride by saturating the reagents with boron fluoride [126] is described, and there is one patent specification relating to the possibility of acylating thiophene in the presence of free BF_3 [152].

Many factors influence the acylation of heterocyclic compounds. Thus, the yield of acyl derivatives depends on the amount of catalyst (within certain limits) and on the rate of its addition to the mixture of reagents. As seen from Table 88 (experiments 19—24), the highest yield of 2-acetylfuran, 77 per cent, is obtained when 14 g $BF_3 . O(C_2H_5)_2$ is added quickly to 1 mole furan and 1·15 moles acetic anhydride. But if the reaction mixture is not treated, as is usual, in half an hour, but left to stand overnight at room temperature, the yield of 2-acetylfuran is decreased to 54 per cent. Therefore the yield of product depends also on the time of the reaction.

In a number of acid anhydrides the acylating activity increases from acetic anhydride to *n*-butyric anhydride, and only in the case of 2,5-dimethylfuran is the change of activity the reverse (experiments 31—33). Benzoic anhydride is less active than the aliphatic anhydrides.

As should have been expected, the more aromatic thiophene is acylated more easily than furan. Thiophene is acetylated with good yield to 2-acetylthiophene in the presence of the complex of BF_3 with acetic acid, and also of catalysts such as $SnCl_4$ and $FeCl_3$. Aluminium chloride scarcely accelerates the acetylation of thiophene, but its coordination compounds with ethyl ether and nitromethane do not accelerate this reaction at all [151].

Table 88. *Acylation of furan, thiophene and their derivatives with acid anhydrides*

No. of expt.	Taken for reaction						Maximum temperature of reaction (°C)	Time of reaction (hr)	Yield of ketone (%)	Literature reference
	Heterocyclic compound	moles	Anhydride	moles	Catalyst	moles				
1	Thiophene	3	Acetic	1	$BF_3 . CH_3OH$	4	50	2·0	70	[149]
2	Thiophene	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	14	110	0·5	73	[150]
3	Thiophene	1	Acetic	1	$BF_3 . 3H_3PO_4$	10	115—124	2·0	63	[155]
4	Thiophene	1	Acetic	1	H_2SO_4	5	110—125	3·0	46	[155]
5	Thiophene	1	Acetic	1	H_2SO_4	5	55	5·0	54	[155]
6	Thiophene	0·5	Acetic	1	H_2SO_4	4	122—127	3·0	43	[155]
7	Thiophene	1	Acetic	1	$p\text{-}CH_3C_6H_4SO_3H$	4	100—125	4·7	62	[155]
8	Thiophene	1	Acetic	1	$(CH_3)_2SO_4$	3	84—96	1·0	0	[155]
9	Thiophene	1	Acetic	1	$HOSO_2F$	10	84—115	2·0	41	[155]
10	Thiophene	1	Acetic	1	$H_2PO_3F . H_2O$	10	95—115	3·0	81	[155]
11	Thiophene	1·5	Acetic	1	$H_2PO_3F . H_2O$	3	93—104	2·0	71	[155]
12	Thiophene	1	Acetic	1	H_3BO_2F	10	110—116	2·0	51	[155]
13	Thiophene	1	Acetic	1	H_3PO_3	4	94—108	2·0	38	[155]
14	Thiophene	2	Acetic	1	$H_4P_2O_7$	2	97	4·0	37	[155]
15	Thiophene	1	Propionic	1·15	$BF_3 . O(C_2H_5)_2$	14	110	0·5	79	[150]
16	Thiophene	1	Butyric	1·15	$BF_3 . O(C_2H_5)_2$	14	110	0·5	89	[150]
17	Thiophene	1 ml	Benzoic	2 g	BF_3 (gas)	—	—	—	40	[126] [149] [154]
18	Furan	3	Acetic	1	$BF_3 . CH_3OH$	4	25	2·0	48	[150]
19	Furan	1	Acetic	1	$BF_3 . O(C_2H_5)_2$	3·5*	110	0·5	44	[150]
20	Furan	1	Acetic	1	$BF_3 . O(C_2H_5)_2$	3·5*	110	0·5	51	[150]
21	Furan	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	3·5†	110	0·5	56	[150]

*Catalyst was added quickly, all together.

†Catalyst was added slowly in the course of 1 hr.

Table 88. *(cont.)*

No. of expt.	Taken for reaction						Maximum temperature of reaction (°C)	Time of reaction (hr)	Yield of ketone (%)	Literature reference
	Heterocyclic compound	moles	Anhydride	moles	Catalyst	moles				
22	Furan	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	6·9†	110	0·5	54	[150]
23	Furan	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	1·5†	110	0·5	54	[150]
24	Furan	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	14*	110	0·5	77	[150]
25	Furan	1	Propionic	1·15	$BF_3 . O(C_2H_5)_2$	14	110	0·5	81	[150]
26	Furan	1	Butyric	1·15	$BF_3 . O(C_2H_5)_2$	14	110	0·5	93	[150]
27	Furan	3	Benzoic	0·44	$BF_3 . CH_3COOH$	3	—	—	55	[154]
28	2,5-Dimethylthiophene	0·5	Acetic	0·58	$BF_3 . O(C_2H_5)_2$	7	100—110	0·5	57	[151]
29	2,5-Dimethylthiophene	0·5	Propionic	0·58	$BF_3 . O(C_2H_5)_2$	7	100—110	0·5	84	[151]
30	2,5-Dimethylthiophene	0·5	Butyric	0·58	$BF_3 . O(C_2H_5)_2$	7	100—110	0·5	93	[151]
31	2,5-Dimethylfuran	1	Acetic	1·15	$BF_3 . O(C_2H_5)_2$	14	100—115	0·5	65	[157]
32	2,5-Dimethylfuran	1	Propionic	1·15	$BF_3 . O(C_2H_5)_2$	14	100—115	0·5	63	[157]
33	2,5-Dimethylfuran	1	Butyric	1·15	$BF_3 . O(C_2H_5)_2$	14	100—115	0·5	60	[157]
34	Thionaphthene	0·5	Acetic	0·58	$BF_3 . O(C_2H_5)_2$	14	114	1·0	67**	[151]
35	Thionaphthene	0·5	Acetic	0·58	$AlCl_3$	38·7	25	16·0	38	[151]
36	Thionaphthene	0·5	Acetic	0·58	H_3PO_4	5	100	2·5	55	[151]
37	Thionaphthene	0·5	Acetic	0·58	I_2	6·4	100	1·0	63	[151]
38	Thionaphthene	0·5	Acetic	0·58	$ZnCl_2$	6·8	100	1·0	45	[151]
39	Thionaphthene	0·5	Acetic	0·58	$SnCl_4$	12·9	115—120	1·0	55	[151]
40	Thionaphthene	0·5	Acetic	0·58	$FeCl_3$	8	104	1·0	70	[151]
41	Benzofuran	0·25	Acetic	0·29	$BF_3 . O(C_2H_5)_2$	3·5	76	0·5	37	[151]

*Catalyst was added quickly, all together.

†Catalyst was added slowly in the course of 1 hr.

**Total yield of 2- and 3-acetylthionaphthenes.

The introduction of halogen atoms into the thiophene or furan ring lowers their capacity for reactions with acid anhydrides and promotes side reactions, for example, the formation of heterocyclic β-diketones, and also α,β-unsaturated ketones [153]. On acetylation 3-methylthiophene gives two isomeric ketones: 3-methyl-2-acetyl- and 4-methyl-2-acetylthiophenes with a preponderance of the first. 2,5-Dimethylthiophene is acylated with good yields of the corresponding acylthiophenes (experiments 28—30). 2,5-Dimethylfuran on acylation forms 3-acyl-2,5-dimethylfurans. In addition the yield of acyl derivatives is slightly lowered from acetic anhydride to butyric anhydride [151]. Such compounds as benzofuran and thionaphthene are comparatively easily acylated by acid anhydrides in the presence of different catalysts, while the first of these is acetylated with acetic anhydride in the presence of small amounts of $BF_3 . O(C_2H_5)_2$ with the formation of only 2-acetylbenzofuran with a yield of 37 per cent, and thionaphthene with acetic anhydride in similar conditions, not only with $BF_3 . O(C_2H_5)_2$ but also with other catalysts, forms a mixture of 2- and 3-acetylthiophenes with a preponderance of the second derivative [151]. For example, in the presence of $BF_3 . O(C_2H_5)_2$ a mixture of two ketones is obtained with a yield of 67 per cent, consisting of 25 per cent 2-acetyl- and 75 per cent 3-acetylthionaphthenes. Isomeric ketones are also obtained with other catalysts ($AlCl_3$, $ZnCl_2$, $SnCl_4$, $FeCl_3$) in approximately the same proportions. It follows from this that the orientation of the acetyl group in benzofuran and thionaphthene depends above all on the nature of the heteroatom.

The acylation of heterocyclic compounds with acid anhydrides in the presence of BF_3 may be carried out with disruption of the ring and the formation of the corresponding ester. Thus, if tetrahydrofuran (14·4 parts), acetic anhydride (30 parts) and 20 per cent BF_3 in ether (1 part) is boiled for 6 hr, butanediol-1,4 diacetate is formed with 72 per cent yield [156].

In carrying out the described acylation reactions it should be taken into account that there is a possibility of *autocondensation of the anhydrides* of the acids, which for some of them takes place easily in the presence of boron fluoride, and in suitable conditions it may be the main reaction of the process. Thus, if boron fluoride is passed into acetic anhydride in the cold to saturation, it is converted almost quantitatively into diacetoacetic anhydride, which is formed as a coordination compound with boron fluoride [115, 158].

On heating the boron fluoride compound of diacetoacetic anhydride with water it is easily decomposed into two molecules of acetylacetone and two molecules of CO_2. It is possible that on this reaction depends the preparation of the highest yield of acetylacetone by the acetylation of acetone with acetic anhydride (Table 87).

When propionic and *n*-butyric anhydrides are saturated with boron fluoride they form a mixture of boron fluoride compounds of mono- and diacylalkylacetic anhydrides with a predominance of the first. When they are decomposed a mixture of mono- and diketones is obtained. The boron fluoride compound obtained from propionic anhydride, on heating with water gives a monoketone with 24·4 per cent yield and a diketone with 11·2 per cent yield. The compound obtained from *n*-butyric acid gives on decomposition a yield of mono- and diketones of 66 and 6·2 per cent respectively.

*iso*Butyric anhydride which has only one hydrogen atom on the carbon atom linked with the carbonyl group, forms with BF_3 a crystalline (m. p. 117—119°) coordination compound of *iso*butyryl-*iso*butyric anhydride $[(CH_3)_2CHCOC(CH_3)_2CO]_2O \cdot BF_3$, which on decomposition gives only the monoketone with a yield of 81·5 per cent [45].

Chloracetic and phenylacetic anhydrides also form coordination compounds with BF_3, but do not undergo autocondensation, and therefore when these compounds are decomposed chloracetic and phenylacetic acids are correspondingly obtained.

Anhydrides of aliphatic carboxylic acids, saturated with boron fluoride and treated with an aqueous solution of sodium acetate, and then heated for 1 hr on the water bath, undergo autocondensation to symmetrical ketones [159]. In this way from propionic, butyric and caproic anhydrides, diethyl-, dipropyl- and diamyl ketones are obtained with a yield of 60, 57 and 64 per cent respectively. 2-Ethylhexanoic anhydride mixed with an equal volume of dichloroethane, saturated with BF_3 and treated with sodium acetate, after stirring for 4 hr gives 1,1′-diethyldiamylketone with 32 per cent yield.

Acylation of Cyclic Compounds with Haloanhydrides of Acids

The investigations, at present very few, known from the literature on the use of boron fluoride and its compounds for acylation by acid haloanhydrides show that at the same time the corresponding ketones are obtained with a lower yield than in the acylation by acid anhydrides. If thiophene is heated with benzoyl chloride in the presence of $BF_3 \cdot CH_3COOH$ for 6 hr at 90—95° 2-benzoylthiophene is obtained with a yield of 22 per cent [149]. If thiophene is boiled for 1—2 hr with acetic, propionic, *n*-butyric and benzoic chloroanhydrides in the presence of catalytic quantities of $BF_3 \cdot O(C_2H_5)_2$ 2-acylthiophenes are obtained with a yield of 51, 55, 69 and 38 per cent respectively [157].

Aromatic and heterocyclic compounds are acylated comparatively easily at room temperature or 40—50° by acid fluoroanhydrides in the presence of BF_3 and $BF_3 . O(C_2H_5)_2$. This reaction was studied in detail by L. M. Smorgonskii [160] who found that such compounds as benzene, toluene, ethyl benzene, *m*-cresol and anisole are acylated well by fluoroanhydrides in the presence of BF_3. However, benzoyl fluoride does not acylate benzene in the presence of BF_3 even by heating on a water bath.

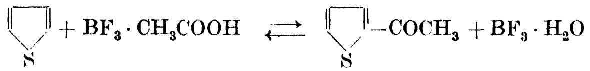
The acylation of furan by benzoyl fluoride in the presence of BF_3 is accompanied by side reactions leading to the formation of large quantities of resins. The expected ketone is therefore obtained with a very poor yield.

Acylation of Cyclic Compounds with Organic Acids

A series of investigations is described in the literature, according to which aromatic hydrocarbons and their derivatives are readily acylated by carboxylic acids in the presence of $AlCl_3$ with the formation of alkylarylketones with a yield of 63—93 per cent. With regard to the use of BF_3 and its compounds for the acylation of cyclic compounds by acids, up to 1946 there was only one patent specification relating to the fact that benzene, toluene, xylenes, naphthalene and other aromatic hydrocarbons form products which are good depressants for lubricating oils when they react with halogenated abietic acid or its related acids in the presence of BF_3 and solvents at room or increased temperature [161].

The acetylation of thiophene with acetic acid in the presence of $BF_3 . O(C_2H_5)_2$ takes place with formation of 2-acetylthiophene [157]:

$$BF_3 \cdot O(C_2H_5)_2 + CH_3COOH \rightleftarrows O(C_2H_5)_2 + BF_3 \cdot CH_3COOH \qquad (I)$$



(II)

The yield of 2-acetylthiophene by this method does not exceed 7 per cent, and therefore the authors are inclined to think that the equilibrium of reaction (I) is strongly displaced to the left.

Carrying out the same synthesis with the complex $BF_3 . CH_3COOH$ (i. e. only reaction II) gives 2-acetylthiophene with a yield of 25 per cent. Attemps to benzoylate naphthalene with benzoic acid in nitrobenzene by saturating with gaseous BF_3 did not give a positive result [26].

Phenols are acylated both by acids and by esters. Particularly good results are obtained when coordination compounds of BF_3 with acids are introduced into the solutions of phenols in double molar quantities, and then the mixture is heated for 2 hr to a temperature of 70° and decomposed with sodium acetate. In this way *p*-hydroxyacetophenone is obtained from phenol and acetic acid with a 91 per cent yield and *o*-hydroxyacetophenone with a 5·9 per cent yield. In similar conditions *p*-hydroxyphenylpropyl ketone is obtained from phenol and propionic acid with a yield of 83·7 per cent and *o*-hydroxyphenylpropyl ketone with a yield of 8·7 per cent. *p*-Methoxyacetophenone is obtained from anisole and acetic acid with a yield of 90·6 per cent.

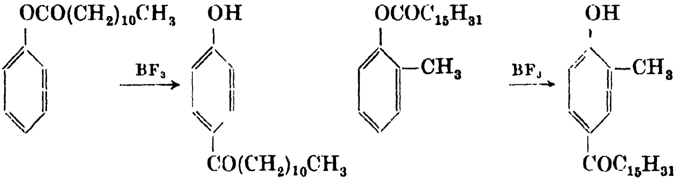
Phenols and cresols are acylated comparatively easily by the higher monobasic acids in the presence of BF_3 [162, 163]. *o*-Cresol with lauric acid and BF_3 form undecyl-4-hydroxy-3-methylphenylketone. Phenol with coconut oil in the same conditions gives *p*-hydroxyphenylundecylketone, but with oleic acid it forms *p*-hydroxyphenylheptadecyleneketone.

α-Naphthol [164] is acylated well by the higher carboxylic acids in the presence of $BF_3 . O(C_2H_5)_2$, and the reaction proceeds with the formation of 2-acyl-1-naphthols only. If an equimolecular mixture of *α*-naphthol and the corresponding acids is heated on a boiling water bath with $BF_3 . O(C_2H_5)_2$ for 4—5 hr the following products are obtained: 2-(*cyclo*hexylbutyryl)-1-naphthol with 80 per cent yield; 2-(phenoxyphenylbutyryl)-1-naphthol with 90 per cent yield; 4-chloro-(2-*cyclo*hexylbutyryl)-1-naphthol with 72 per cent yield and 2-(lauryl)-1-naphthol with 82 per cent yield.

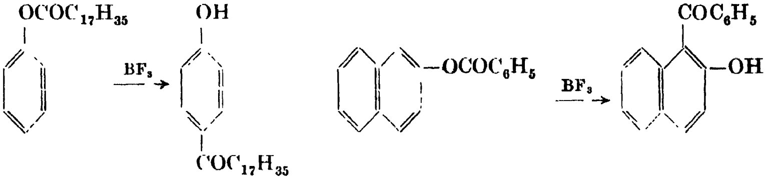
Phenolic esters are more difficult to acylate with acids in the presence of boron fluoride. In conditions in which the acylation occurs easily, they can undergo an isomerization known in the literature as the Fries rearrangement with the formation of hydroxyphenylalkylketones. This isomerization takes place particularly easily in the presence of solvents, and the acyl residue is directed mainly into the *p*-position. If, for example, phenyl acetate fluoroborate is heated for 7 hr at 70—73° with $BF_3 . O(C_2H_5)_2$, *p*-hydroxyacetophenone is obtained with a yield of 51·5 per cent. In nitrobenzene this same reaction (in the course of 80 min) takes place with the formation of *p*-hydroxyacetophenone with a yield of 52·7 per cent, but in fluoroboroacetic acid after the same time the yield of isomerization product is 89·5 per cent [132].

Cresyl acetate at 85° isomerizes to *o*-acetyl-*p*-cresol with a yield of 57·9 per cent.

Esters of the higher acids containing 10—18 carbon atoms in the molecule isomerize in a similar way [163, 164]. For example, if 276 g phenyl laurate (I) are heated for 6—8 hr at 80—90° with 68 g BF_3, undecyl-*p*-hydroxyphenylketone (II) is formed. *o*-Cresyl palmitate (III) isomerizes to pentadecyl-4-hydroxy-3-methylphenyl ketone (IV), and phenyl stearate (V) is converted into heptadecyl-*p*-hydroxyphenyl ketone (VI):



(I) (II) (III) (IV)



(V) (VI) (VII) (VIII)

2-Naphthylbenzoate (VII) in nitrobenzene, when treated with excess of BF$_3$, isomerizes to phenyl-2-hydroxy-1-naphthyl ketone with a yield of 34 per cent [126].

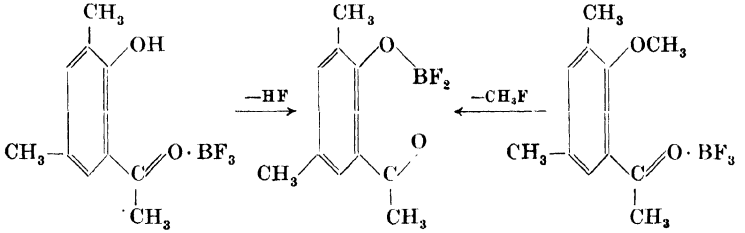
Phenyl formate in the presence of BF$_3$ does not give the expected *p*-hydroxybenzaldehyde, but forms more complex condensation products which are obtained as a result of the isomerization of *p*-hydroxybenzaldehyde. Mesityl acetate, in which there are no active positions for the introduction of the acetyl residue, does not undergo the Fries rearrangement, and on heating for 45 hr at its melting point (124·5°) it is recovered unchanged as a boron fluoride compound.

In connection with this it may be pointed out that when it acts on mesityl acetate the catalyst AlCl$_3$ produces a migration of one methyl group and thus permits isomerization to take place with the formation of acetohemellitenol.

As the experimental data show, the Fries rearrangement in the presence of BF$_3$ takes place not only on heating phenyl esters of carboxylic acids to their melting point, but also when these compounds are in the crystalline state. Thus, the boron fluoride compound of asymmetrical *m*-xylenyl acetate is converted into *o*-aceto-asymm.-*m*-xylenol with a yield of 81·2 per cent after standing for three days at room temperature.

Thus the formation of hydroxyphenylalkylketones from phenols and acids in the presence of BF$_3$ evidently takes place not by the direct introduction of the acyl residue into the benzene ring, but through the formation of phenyl esters of carboxylic acids as intermediate products.

One of the main advantages of BF_3 over other catalysts ($AlCl_3$, $BiCl_3$, $SbCl_5$) is that it does not give fluoroanhydrides on acylation with acid anhydrides and does not form HF when phenols are acylated by acids, or RF when alkyl ethers of phenols are acylated in all reactions in which an acyl enters the *p*- or *m*-position. But if the acyl (in our example, acetyl) group enters the *o*-position to the OH or OR group, then HF or RF splits off even at low temperatures in the presence of BF_3, and a very stable intracomplex compound is obtained according to the scheme



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CHAPTER XII

VARIOUS REACTIONS WHICH ARE CARRIED OUT IN THE PRESENCE OF BORON FLUORIDE

1. THE CRACKING REACTION

UNTIL recently there were no original investigations published dealing with the cracking of hydrocarbons in the presence of boron fluoride, but many patent claims had been made on the use of boron fluoride and its coordination compounds for cracking crude petroleum and for decomposing hydrocarbon oils, kerosene and other high molecular hydrocarbons [1—8].

If hard petroleum fractions are heated in the presence of BF_3 to a temperature above 300° and under pressure, the main decomposition products are unsaturated benzines [1, 9]. Thus, from the fraction boiling above 300°, in the presence of 5 per cent BF_3 at a temperature of 380° and a pressure of 150 atm, a product is obtained, 75 per cent of which boils up to 250°. In the presence of 10 per cent $BF_3 . O(C_2H_5)_2$ at 400° and atmospheric pressure, the volatile fractions of the benzines obtained amount to 60 per cent [1]. On heating the kerosene fraction which boils within the range 150—250° with the same amount of butane fraction and with 5 per cent by weight $CoCl_2$, 5 per cent HF and 1 per cent BF_3, at a temperature of 500° and a pressure of 2 atm, benzine with an octane number of 77 is obtained with an 80 per cent yield [10]. By heating the naphthenic petroleum fractions, which boil above 125°, in the presence of BF_3 they are converted into *iso*butane [11]. If the process is carried out in the presence of BF_3 and HF, *iso*butane is obtained with a higher yield [12]. In one of the patents [13] it is recommended that BF_3 be used in combination with $Al_2O_3 . SiO_2$ as a catalyst for the preparation of benzine by cracking gas oil. In contrast with these data, M. Ya. Friedman [14] in his work showed that when kerosine was cracked in the presence of BF_3 no change was detected in the fractional composition and in the specific gravity of the original kerosine.

Ya. M. Paushkin and Yu. S. Lipatov [15, 16] investigated the cracking of diesel fuel at atmospheric pressure on carbon and aluminium silicate in the presence of BF_3. The raw material was passed through the solid catalyst at a volume rate of 0·24 hr^{-1}. Boron fluoride (10 per cent of the raw material), which was prepared by the thermal decomposition of the BF_3 complex with anisole, was supplied continuously to the reaction vessel.

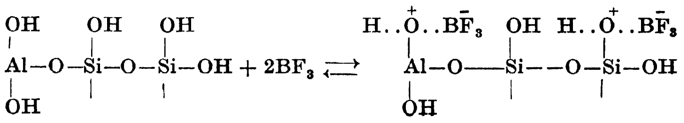
When cracking on carbon at 350—360° in the presence of BF_3 a quite unexpected phenomenon was observed, namely an inhibition of the cracking. In cracking in the presence of BF_3, the yield of benzine was decreased to almost a half, in comparison with cracking on carbon alone, the bromine number of the cracking-benzine was considerably reduced, and the yield of cracking gas and content of unsaturated hydrocarbons in it diminished. Cracking at 350—450° in the presence of BF_3 gives a distillate heavier than the original raw material. This phenomenon is explained by the condensing, polymerizing and alkylating effect of boron fluoride, which leads to a thickening of the original raw material, or a decrease in the extent of its decomposition. Typical results of the cracking are given in Table 89.

Table 89. *Cracking in the presence of boron fluoride on carbon*

Catalyst	Temperature of cracking (°C)	Yield of benzine boiling up to 200° (%)	Bromine value of benzine	Cracking gas	
				Yield of gas per 100 g raw material (l)	Unsaturated hydrocarbon content (%)
Carbon	460	39	20	5·6	8
Carbon + BF_3	460	11	10	2·2	5
Carbon + BF_3	500	41	44	14·0	—
Carbon + BF_3	500	22	9	—	—
Carbon + BF_3	560	31	60	17·6	29
Carbon + BF_3	560	17	40	9·7	19

Cracking on an aluminium silicate catalyst in the presence of BF_3, when the experiment is carried out under the same conditions as on carbon, has quite another character. The boron fluoride to a considerable extent activates the aluminium silicate catalyst, raising the yield of benzine by 15—45 per cent depending on the cracking temperature, while benzine of lighter composition is obtained. Cracking-benzine, prepared on aluminium silicate in the presence of boron fluoride, has a smaller octane number determined by the motor method (Table 90).

During the cracking, activation of the aluminium silicate catalyst by the boron fluoride is observed, similar to that which takes place in the case of sulphuric and phosphoric acids in alkylation and polymerization reactions. This phenomenon may be explained by the formation on the surface of the catalyst of BF_3 complexes with the hydroxyl groups of silicic acid and aluminium oxide:



$$\begin{array}{l}\mathrm{OH}\qquad\mathrm{OH}\qquad\mathrm{OH}\\ \mathrm{Al{-}O{-}Si{-}O{-}Si{-}OH}\\ \mathrm{OH}\end{array} + 2BF_3 \rightleftarrows \begin{array}{l}\mathrm{H..\overset{+}{O}..\overset{-}{B}F_3}\quad\mathrm{OH}\quad\mathrm{H..\overset{+}{O}..\overset{-}{B}F_3}\\ \mathrm{Al{-}O{-}Si{-}O{-}Si{-}OH}\\ \mathrm{OH}\end{array}$$

Table 90. *Cracking in the presence of boron fluoride on aluminosilicate catalyst*

Catalyst	Temperature of cracking (°C)	Cracking-benzine, boiling up to 200°			Content of unsaturateds in cracking gas (%)
		Yield calc. on original raw material (%)	Bromine value	sp. gr. d_4^{20}	
Aluminosilicate	400	48	10	0·806	18
Aluminosilicate + BF_3	408	60	6	0·786	5
Aluminosilicate + BF_3	440	48	18	0·809	12
Aluminosilicate + BF_3	440	60	11	0·793	9
Aluminosilicate + BF_3	512	54	18	0·838	7
Aluminosilicate + BF_3	510	61	8	0·819	4

Some polymerization products of olefines and diolefines are depolymerized in the presence of boron fluoride on heating to high temperatures [17—22]. Thus, by pyrolysis of the corresponding polymeric products in the presence of BF_3 or $(C_2H_5)_2O \cdot BF_3$ at a temperature of the order of 900°, butadiene is obtained with a good yield [19].

Rubbers dissolved in aromatic hydrocarbons and treated with BF_3 undergo depolymerization [20—22]. Cyclic ethers, for example 4-methyl-1,3-dioxane [23] are decomposed in the presence of BF_3 with subsequent polymerization of the decomposition products. Natural resins, such as colophony [24], are decarboxylated on heating with BF_3.

2. DEALKYLATION AND DISPROPORTIONATION

Alkylbenzenes (*n*-propyl-, *iso*propyl-, methylethyl-, diethyl-, di*iso*propyl-, *iso*butyl- and amyl-benzenes), on treatment with $BF_3 \cdot HF$ in the presence of small amounts of water at a temperature of 300—350° and increased pressure, are dealkylated to benzene or monoalkyl benzenes [25]. 4-Alkyl-2,6-dihalophenols dealkylate particularly easily in the presence of BF_3 to 2,6-dihalophenols [26]. Xylene (175 g), with a large excess of benzene (529 g) in the presence of HF (100 g) and BF_3 (50 g) at a temperature of 300° and a pressure sufficient to keep the reagents in the liquid phase, is 61 per cent converted into toluene [27]. The reaction may be represented as

$$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$$

Ethyl benzene in the presence of BF_3 and HF disproportionates into *m*-diethyl benzene and benzene [28], and xylene into mesitylene and benzene [29].

Catalysts based on boron fluoride promote the decomposition of paraffinic hydrocarbons, with subsequent condensation. Great interest began to develop in this reaction recently when the possibility was demonstrated of using it for the conversion of the lower hydrocarbons of the propane, butane, pentane type to higher hydrocarbons, i. e. for the catalytic conversion of saturated gases and pentane to *iso*butane and benzine. In many patents it is suggested that propane can be converted to *iso*butane by means of a liquid catalyst, consisting of HF and BF_3, at 25—200° and a pressure of 3·5—40 atm [30, 31]. The same catalyst is recommended for the preparation of butanes from propane and pentane [32], and also from the pentane hydrocarbons [33, 34, 35] corresponding to benzines. Octane is obtained from dodecane and *iso*butane [36]. In a similar way hydrocarbons of heavy oils can be converted with *iso*butane into high octane benzines [37]. The essence of the process of these conversions consists in the preliminary decomposition of high-molecular paraffinic hydrocarbons and subsequent alkylation of the isoparaffins with the olefines formed when the paraffins decompose.

The first detailed investigation of the catalytic conversion of propane into *iso*butane, of butane into *iso*butane and of pentane into higher hydrocarbons and *iso*butane by means of the catalyst $BF_3 + HF$ was published in 1951 [38]. The reaction was carried out at an increased pressure of the order of 10 atm, but for propane of about 65 atm, and at a temperature of 42—45°. The process was studied in a small experimental plant with a reaction vessel of 2·8 l. capacity.

It is interesting to note that the separate components of the catalyst, BF_3 and HF, in the dry state do not corrode steel, but the BF_3—HF catalyst causes severe corrosion; owing to this, nickel, copper, brass and Monel metal were used for the reaction apparatus. For the gaskets polyfluoroethylene was used, because all other plastics are unstable in these conditions.

The reaction was carried out in a reaction vessel lined with Monel metal and provided with copper supply tubes. To make close contact of the catalyst with the hydrocarbons, mixing of the reaction mixture was carried out with stirrers of the turbine type. The hydrocarbons and the hydrogen fluoride were put in the reaction vessel under pressure, and the boron fluoride was added from a cylinder until the required partial pressure was reached. After the reaction the emulsion of hydrocarbons with the catalyst was separated, the hydrocarbon layer washed, dried and subjected to low temperature rectification. After the separation of the hydrocarbons the mixture was distilled with the object of recovering the catalyst, because the volatile BF_3 and HF are separated from the inactive complexes with hydrocarbons at the same time.

The dissolved catalyst was separated from the hydrocarbons by distillation (about 0·6—0·7 per cent of the BF_3—HF catalyst is dissolved in the hydrocarbons).

The disproportionation of propane was carried out under a pressure of 47 atm at 85° in the course of 2 hr with 100 per cent by volume HF in relation to the liquid propane, at a partial pressure of BF_3 of 10·5 atm; this partial pressure corresponds to 53·7 per cent by weight of boron fluoride in relation to the hydrocarbons. As a result of the disproportionation of the propane the data given in Table 91 were obtained.

Table 91. *Composition of disproportionation products*

Composition of original hydrocarbon	Yield (%)	Composition of hydrocarbons after reaction			
		Ultimate product	Yield (%)	Products of disproportionation	Yield (%)
Propane	97	Propane	88·2	Ethane	5·7
Propylene	0	Lighter than propane	0·5	*iso*Butane	82·8
Ethane	Traces	*iso*Butane	11·2	Hydrocarbons in catalyst	11·5
*iso*Butane	3	Losses	0·1		

Thus, propane may be converted into *iso*butane at one operation with a conversion of about 10 per cent, and this must, no doubt, be of considerable interest.

Contact of BF_3—HF with *n*-butane gives mainly *iso*butane with the formation of 4—8 per cent of higher-boiling hydrocarbons (Table 92).

Table 92. *Isomerization and disproportionation of butane with the catalyst* $BF_3 + HF$

Conditions	Experiment			
	1	2	3	4
Temperature (°C)	50	50	50	50
Pressure (atm)	27	24	12·5	24
Duration of reaction (min)	120	30	30	30
HF, % by volume of the butane	50	100	100	100
Partial pressure of BF_3 (atm)	21	14	50	14
BF_3, % by weight of the butane	71	7·5	1	7·7
Composition of charge (%)				
*iso*Butane	1	16	16	16
n-Butane	7	81·8	81·5	84
Butylene	2	2·2	2·5	0
Composition of products of the reaction (%)				
*iso*Butane	29	53	43	17
Hydrocarbons lighter than C_4	2·7	0·7	0	0
Hydrocarbons heavier than C_4	3·4	8·4	1·3	0

Butylene promotes the conversion of butane to *iso*butane; thus, in experiment 2 a considerable conversion of butane to *iso*butane was observed in the presence of 2·2 per cent butylene; but in experiment 4, where there was no butylene in the raw material, other conditions being equal, hardly any conversion was observed. The conversion to *iso*butane reached 43 per cent while the thermodynamic equilibrium at the temperature of the experiment corresponded to a content of 68 per cent *iso*butane.

The partial pressure of BF_3 in the reaction system exerts a substantial influence. Thus, on doubling the partial pressure (from 10·5 to 21 atm) the isomerization of *n*-butane to *iso*butane increases from 11 to 29 per cent.

The disproportionation of pentane with the BF_3—HF catalyst takes place with conversion to higher hydrocarbons to the extent of 24 per cent and the formation of a large amount of *iso*butane (Table 93). The temperature of the reaction exerts a substantial influence on the disproportionation of *n*-pentane; thus at 43° the reaction hardly takes place at all and the conversion of pentane amounts to 3 per cent, but at 85° it reaches 79·2 per cent. However, the addition of amylene, which accelerates the reaction, in a quantity of 2 per cent makes it possible to carry it out even at 32°. In the gases which are obtained in the conversion there is about 55 per cent of *iso*butane.

Table 93. *Disproportionation of* n-*pentane in the presence of the catalyst* $BF_3 + HF$

Conditions	Experiment			
	1	2	3	4
Temperature (°C)	85	43	65	32
Pressure (atm)	21	14	17·5	14
Duration of reaction (min)	30	30	30	30
HF, % by volume of the pentane	50	100	100	100
Partial pressure of BF_3 (atm)	10·5	10·5	10·5	10·5
BF_3, % by weight of the pentane	8·3	37·7	32·0	32·3
Amylene content (%)	0	0	0	0
Composition of products of reaction (weight %)				
Propane	12·1	0	1	0·8
*iso*Butane	29·4	1·0	12·0	21·0
n-Butane	12·7	0	0	3·3
*iso*Pentane	18·3	23·6	56·0	34·7
n-Pentane	2·5	73·4	7·1	14·0
Hydrocarbons heavier than C_5	16·8	2·0	23·0	24·0
Disproportionation of pentane (%)	79·2	3·0	36·9	—

Heptane also undergoes conversion on contact with BF_3—HF with the formation of low boiling products and approximately 15—16 per cent of hydrocarbons boiling higher than heptane; the conversion of heptane at 85° reaches 51·6 per cent, and at 65° 8·7 per cent. Thus, in this case the conversion is lower than with pentane.

Ya. M. Paushkin [39], and also A. V. Topchiev and I. M. Tolchinskii, found that the disproportionation of pentane proceeds well in the presence both of aluminium chloride and of aluminium silicate [39a]. The best temperature for the reaction with $AlCl_3$ is 80° and the duration of the reaction is 1 hr. In addition, the conversion of pentane to liquid products with a boiling point higher than pentane reaches 30—40 per cent, but the gas formed contains about 60 per cent *iso*butane. The hexane fraction of the liquid products consists of 35 per cent 2,2-dimethylbutane, 48 per cent 2-methylpentane, 2·5 per cent 3-methylpentane, 3 per cent *n*-pentane and 11·5 per cent of other hydrocarbons. In the presence of $AlCl_3$ this reaction may also be carried out at 5—20°, but with a long time of contact. With aluminium silicate the reaction takes place at 400—500°.

On comparing the results of the experiments on the disproportionation of pentane with BF_3—HF and $AlCl_3$, it is possible to draw the conclusion that hydrogen fluoride with boron fluoride behaves in a similar way to aluminium chloride.

The disproportionation reaction may be considered as a conjugate reaction of cracking and alkylation. In the cracking, energy is absorbed which is compensated for by the energy produced in the subsequent alkylation, and therefore the reaction becomes possible at low temperatures. For pentane the reaction takes place according to the equations:

$$2C_5H_{12} \longrightarrow \left| \begin{array}{l} \longrightarrow C_6H_{14} + C_4H_{10} \\ \longrightarrow C_7H_{16} + C_3H_8 \\ \longrightarrow C_8H_{18} + C_2H_6 \\ \longrightarrow C_9H_{20} + CH_4 \end{array} \right.$$

3. SEPARATION AND PURIFICATION OF HYDROCARBONS BY MEANS OF BORON FLUORIDE COMPOUNDS

Aluminium halides with hydrohalic acids form complexes with aromatic hydrocarbons of the type $HAlX_4$. ArH.

It was found [40—42], that the system BF_3—HF also forms similar complexes with aromatic hydrocarbons and sulphur compounds. This makes possible the removal of aromatic and sulphur compounds from the petroleum products with the help of boron fluoride and hydrofluoric acid. After separation from the hydrocarbon layer, the complexes formed are broken down by heating, as a result of which the BF_3 and HF are completely recovered and the extracted compound is separated.

On this property is based the use of BF_3 with HF as a medium for the desulphurization of petroleum products, with the object of preparing high-quality kerosenes and lubricating oils from low-quality petroleums rich in sulphur compounds, and also for purifying other natural high-molecular products [43—47]. The extraction is carried out by vigorous stirring of the petroleum products with liquid hydrogen fluoride under pressure of boron fluoride [41] and separation of the extracted layer from the hydrocarbon layer. The aromatics are extracted usually by this agent, just as with compounds containing sulphur (the extracted layer contains 71—97 per cent of aromatic compounds). The aromatics are finally treated by heating, because the volatile BF_3 and HF are easily distilled off. It is recommended that HF in amount 10—29 per cent of the volume of the petroleum product be used for the extraction. The degree of removal of sulphur depends on the amount of BF_3 used. But it is usually complete enough. For example, by the method described the sulphur content may be decreased from 0·85 per cent in the original raw material to 0·11 per cent in the refined product, or from an original 2·26 per cent to 0·30 per cent sulphur in the refined product. Moreover, in addition to the removal of sulphur, purification of the products also takes place because the coloured matter separates into the extracted layer.

Desulphurization of hydrocarbon mixtures also occurs with the help of hydrogen fluoride alone, but in this case it appears less complete. The addition of BF_3 increases the extractive capacity of the HF several times. For example, when *n*-heptane containing 8·9 per cent by weight of phenyl sulphide is treated with hydrogen fluoride, the phenyl sulphide is 15 per cent extracted, but when it is treated with a BF_3—HF mixture the sulphide is 93 per cent extracted [40]. Extraction of sulphur from crude petroleums by HF in the presence of 5·3 per cent by weight of BF_3 increases from 34 per cent (in the presence of HF alone) to 91 per cent of the potential possible sulphur content [45]. In addition the aromatics are also removed.

Free boron fluoride [48], boron fluoride monohydrate [49], boron fluoride ethyl etherate [48, 50, 51], the compound $BF_3 \cdot 2CH_3COOH$ [48] and boron fluoride with alkane sulphonic acids [48] are also used for desulphurizing petroleum products (petroleum oils, gasoline) and separating aromatic hydrocarbons from paraffins. For example, if a petroleum oil having an unpleasant odour, an orange colour and containing 0·78 per cent sulphur, with a mercaptan number of 48, is treated with 0·488 mole methane sulphonic acid and 0·107 mole BF_3, it gives an oil of pale yellow colour, almost without odour, having a mercaptan number of 16 and containing 0·29 per cent sulphur [48].

Since aromatic hydrocarbons form with the system BF_3—HF complexes of different stability, this makes it possible to separate aromatic hydrocarbons and their isomers from each other. For example, *m*-xylene easily forms a complex with the system BF_3—HF, but the *o*- and *p*-isomers form these complexes with more difficulty, and therefore *m*-xylene may be separated from the mixture as a complex and recovered by heating the latter to 40—70° (BF_3 and HF also distil off), or by dissolving it in water [41, 52]. In this way 95 per cent of the *m*-xylene may be separated from a mixture of isomers, while for the extraction it is desirable to use a neutral solvent similar to petroleum ether.

When stirred with liquid HF under pressure of BF_3 xylenes are quickly transferred to the acid layer, forming a complex which is probably formed according to the following scheme :

$$HF + BF_3 + C_6H_4(CH_3)_2 \rightarrow BF_3 . HF . C_6H_4(CH_3)_2$$

It was found that in the complex one molecule of boron fluoride joins on to one molecule of xylene. The complex dissolves in excess hydrofluoric acid and thus separates from the hydrocarbon layer.

Measurement of vapour pressure showed that the stability of the complexes with isomers of xylene may be characterized by the ratio meta : ortho : para = 20 : 2 : 1. As the complex with *m*-xylene is the most stable, it is formed first on the entry of the boron fluoride and may be separated.

Boron fluoride, in the form of complex compounds with alcohols, ethers and other compounds containing oxygen, is recommended for the purification of the products of alkylation (for example, of *iso*butane by propylene) from alkyl fluorides [53, 54], which are formed in the alkylation reaction when the catalyst HF is used.

By means of boron fluoride it is possible to separate mixtures of carboxylic acids and their esters owing to the formation of coordination compounds of different stability [55].

On treating compounds of the general formula

$$p\text{-}ROC_6H_4CHR'CH(OH)C_6H_4OR\text{-}p$$

with boron fluoride or its complexes, dialkoxystilbenes or their substituted derivatives are obtained [56].

m-Dioxanes or *m*-dioxolanes and their derivatives, with methanol in the presence of BF_3, are decomposed into glycols [57]. Aromatic amines, with water in the presence of BF_3 on heating to above 200°, form phenols [58, 59].

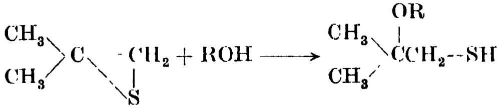
Boron fluoride as ethyl etherate accelerates the reaction of unsaturated hydrocarbons with mercuric acetate [60, 61]. Thus, *cyclo*hexene with

$Hg(OCOCH_3)_2$ in petroleum ether in the presence of $BF_3 . O(C_2H_5)_2$ forms 1-acetoxy-2-acetoxymercury*cyclo*hexane with 91 per cent yield [60]. *trans*-Stilbene and $Hg(OCOCH_3)_2$ in methanol with $BF_3 . O(C_2H_5)_2$ is converted into $[C_6H_5CH(OCH_3)]_2$ [61]. Benzene with $Hg(OCOCH_3)_2$ and BF_3 gives phenylmercury acetate $C_6H_5HgOCOCH_3$ [62]. Polyalkyl lead with dihalogen derivatives of olefines in the presence of BF_3 forms compounds of the general formula $(R_3Pb)_2R'$, which are difficultly volatile antidetonators [63]. For example, on heating a mixture of $Pb(CH_3)_4$, $C_2H_4Br_2$ and BF_3 the compound $(CH_3)_3PbCH_2CH_2Pb(CH_3)_2CH_2CH_2Br$ is obtained.

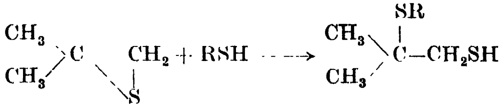
tert.-Mercaptans in the presence of BF_3 are converted into sulphides [64]. Thus, *tert.*-butylmercaptan with BF_3 is converted into di-*tert.*-butyl sulphide. When mercaptans and alkyl halides are worked up in the presence of BF_3, alkyl sulphides are also formed [65].

tert.-Alkyl halides with hydrogen sulphide in the presence of BF_3 give *tert.*-mercaptans. For example, *tert.*-chlorobutane and hydrogen sulphide with BF_3 give *tert.*-*iso*butylmercaptan [66].

*iso*Butylene sulphide with alcohols in the presence of $BF_3 . 2CH_3COOH$ is converted into alkoxythiols [67] according to the reaction



Sulphides of olefines with mercaptans in the presence of BF_3 or $BF_3 . O(C_2H_5)_2$ form primary and tertiary mercaptans or β-mercaptothioethers [68, 69]:



*cyclo*Hexene sulphide with mercaptans gives only *sec.*-mercaptans [68].

Mercaptans can be condensed with phenol alcohols in the presence of BF_3 [70]. If saturated hydrocarbons are treated with 1—20 per cent of phosphorus sulphides (for example, P_2S_5) in the presence of BF_3 at a temperature of 375—425°, products are obtained which are readily soluble in hydrocarbons and are used as additives to lubricating oils, or as corrosion inhibiting lacquers [71]. Similar types of additives or depressants for lubricating oils are obtained on treating alkylarylketones of the general formula RCOAr with sulphur monochloride or dichloride in the presence of BF_3 [72].

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